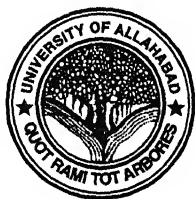


THERMODYNAMIC AND EQUATION OF STATE STUDIES OF FLUIDS

Thesis Submitted to the **UNIVERSITY OF ALLAHABAD**
for the Degree of Doctor of Philosophy in Science



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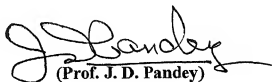
**Department
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**THIS INVESTIGATION WORK
IS
DEDICATED
TO
MY HONOURABLE
DADA JI
PADMAKAR MISHRA**

CERTIFICATE

This is to certify that **MR. RAJESH KUMAR MISHRA** has fulfilled all the requirements for the submission of the D.Phil. thesis entitled "**THERMODYNAMIC AND EQUATION OF STATE STUDIES OF FLUIDS**" to the University of Allahabad. This is a record of the candidate's own effort under my guidance and supervision.



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Most of all, I would like to place on record in a very special manner my deepest regards and well - wishes to members of the Mishra family and my elder brother who provided not only financial but also moral and emotional support.

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PREFACE

Thermodynamic and transport properties of fluid and fluid mixtures play a very important role in understanding the nature of intermolecular interactions, internal structure and physicochemical behavior of liquids and liquid mixtures. Since experimental measurements of various properties become progressively difficult and cumbersome and even impossible in some cases, many remarkably successful attempts for predicting the various parameters and properties of the multicomponent systems from the knowledge of the properties of their contributory binary systems have been made. In addition to this, an interesting attempt has been made to extend the theoretical formalisms and to utilize various equations of state to predict the thermodynamic properties of binary and multicomponent liquid systems. Various empirical, semi-empirical and statistical mechanical theories are presented in modified form to study these properties for fluid mixtures. In the entire work presented here an attempt has been made to theoretically evaluate various thermodynamic properties like ultrasonic velocity, isothermal compressibility, internal pressure, Gruneisen parameter, refractive indices and the non-linearity parameter of binary and multi component liquid mixtures using some experimentally determined properties existing in literature.

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CHAPTER-I

INTRODUCTION

Liquids and dense fluids are usually considered to be complicated on a molecular scale, and a satisfactory theory of liquids only began to emerge in the 1960s. However, they show a number of simple regularities, some of which have been known for years without any theoretical basis. Some of the known regularities have been given a theoretical basis, but others remain completely empirical. Although the theoretical understanding of the liquid state is constantly improved, most phenomena occurring at high pressure have not yet received theoretical support. At present, current theories have successfully explained only few regularities observed in liquids at high pressures. For practical purposes most properties of liquids are described by phenomenological equations¹⁻⁸. Experimental PVT or $P\rho T$ data of liquids have been widely used, and still in progress, for deriving the thermodynamic and transport properties of liquids and liquid mixtures. Experimental results of isothermal compressibility, thermal expansivity, heat capacity etc are further used to test the performance and validity of particular equation of state. Also, the equations of state based on statistical- mechanical theory have been examined utilizing the experimental properties of liquids and liquid mixtures. During recent years importance of equation of state in deducing the thermodynamic (compressibility, thermal pressure coefficient, Grüneisen parameter, non-linearity parameter etc) properties and transport properties (viscosity, thermal conductivity and diffusion coefficient) of fluids and fluid mixtures. Hard sphere equations of state have also been successfully utilized to predict various thermodynamic properties of binary and higher order liquid mixtures during recent years⁹⁻²². Also sound velocity in conjunction with equation of state has been widely employed to estimate a number of equilibrium and transport properties of fluids and fluid mixtures^{23, 24}.

Nature of intermolecular interaction and thermodynamic behaviour of binary and multicomponent systems have considerable significance in thermodynamics. Intermolecular forces on the whole are a very wide subject in the study of binary and multicomponent systems. Various detailed theories and discussions in this regard have been given by Hirschfelder²⁵, Margenau²⁶, Kihara²⁷ Rowlinson²⁸ Hildebrand and coworkers²⁹ and Moelwyn-Hughes³⁰. In recent years⁹⁴⁻¹⁰⁷ considerable advancement in theoretical and experimental investigations has been made for thermodynamic

properties of fluid mixtures. Mostly, in case of simple liquids, the values of thermal conductivity are greater than those at low-pressure and same temperature. There is very small effect of pressure, and an increase in temperature usually decreases the thermal conductivity values. The difference between values of transport properties in gas phase and the values in liquid phase indicates a distinct change in mechanism of energy or momentum or mass transfer. In the gas phase the molecules are relatively free to move about, and transfer momentum and energy by a collision mechanism. In the liquid state, there is little wandering of individual molecules so that energy and momentum are primarily exchanged by oscillation of molecules in the shared forced field surrounding each molecule. . Various workers like McLaughlin⁵², Ewing et al⁵³ etc presented different theories to estimate the thermal conductivities of pure liquids. But these theories were less accurate and less useful for pure fluids. Therefore appropriate techniques must be applied for engineering applications. Extensive application of Flory's statistical theory^{63,65} for the computation of various excess thermodynamic functions have been used by numerous investigators⁵⁴⁻⁵⁸. Flory explored the statistical theory starting from a reduced equation of state and using comparatively simpler partition function suitable for liquids. Recently an attempt has been made to use the Flory statistical theory to evaluate thermal conductivity of pure liquids using velocity of those pure liquids using velocity data. In subsequent studies Flory statistical theory has been extended to ternary liquid mixtures. In addition to this recently proposed Marcus¹⁴⁸ relation and extended Sutherland Wassiljewa¹⁴⁷ equation for gases have been employed to ternary liquid mixtures. Li's¹⁴⁶ equation and several other empirical relations proposed for viscosity has been used for evaluation of thermal conductivity of binary liquid mixtures.

In recent past ^{25,32,92-93} numerous theories have been developed to study the thermodynamic properties, which relates properties of fluid mixtures with measurable macroscopic properties of pure components. One of these, Flory theory, was initially derived to explain the thermodynamic properties of n- alkane mixtures and was successfully to non- polar molecules differing in size and shape, and has been employed to systems which are simple and complex fluid mixtures ^{38,41,43-45}. Further

improvement to this theory for fluid mixtures have been done by Prigogine- Flory by considering the some of three contributions, a combinatorial term, an interaction term arising from the difference in chemical nature of the two components and free volume contribution. Better understandings of the nature of these contributions have been provided by Patterson and his coworkers⁴⁵⁻⁴⁷. Flory- Patterson theory has also been applied successfully for evaluation of various thermodynamic properties of binary mixtures of ionic liquid⁴⁸⁻⁵⁰, liquid metal⁵¹, and ternary ionic melts. The general description of the fluid mixtures with in statistical mechanics represents a difficult problem. But simplicity and precision in the prediction of various thermodynamic properties makes the Flory statistical theory more interesting. In recent past, Flory statistical theory of binary liquid mixtures^{53-61,74-77} has also been successfully employed to multicomponent liquid mixtures for calculating activity⁸⁸, surface tension^{62-65,79-81}, excess volume^{82,83}, viscosity⁸⁴⁻⁸⁶, sound velocity⁸⁷⁻⁸⁹ and related properties^{90,91}.

Experimental measurements of refractive index and dielectric permittivity of liquid mixtures have gained much importance during recent past¹³⁰⁻¹³⁸. The measurements were made mostly in binary mixture¹²⁵⁻¹⁴¹ except few in ternary systems^{132, 133} for dielectric permittivity. Comparatively refractive index studies of a number of binary liquid mixtures^{130,131,135,136,139,,141}, some ternary mixtures^{141,142} and very few quaternary systems^{143,144} have been reported earlier. Refractive index data were analyzed in terms of various mixing rules suggested by different workers from time to time¹⁴²⁻¹⁴⁵.

During earlier studies it was assumed that amplitudes of propagating waves were infinitely small and as a result of this, the characteristics of both the medium and ultrasonic waves propagating through it should not be affected by another. But for all practical purposes it is found that intensity or amplitude of sound waves coming out from transducer are finite. However, the measurements related to ultrasonic propagation becomes unreliable³⁴ when sound waves of finite amplitude are made to propagate in fluids, because nonlinear effects like acoustic streaming and distortion of wave form occur due to greater attenuation of high frequency constants compared to low frequency ones. These non-linearity effects represented by nonlinear terms are

well studied by the factor (B/A) known as nonlinearity parameter. A number of experimental and theoretical studies have been carried out on the nonlinearity parameter of liquids making use of phenomenological equation⁶⁷⁻⁶⁹ or thermodynamic methods⁷⁰⁻⁷¹. Sehgal et al⁷² computed B/A values for alcohol- water mixture and discussed variation of B/A with alcohol concentrations for five different alcohols on the basis of solute-solvent interactions and quasi static structure of water. Tong and Dong⁷³ computed B/A values for pure liquids by making use of Schaaffs velocity equation. During the recent years, several workers¹²⁶⁻¹²⁹ have reported ultrasonic velocity, non-linearity parameter and other thermodynamic parameter in a number of pure liquids and binary liquid mixtures. It is possible to obtain certain information about the physical attributes of liquids such as internal pressure, intermolecular spacing etc from the values of nonlinearity parameter. The nonlinearity parameter plays a significant role in nonlinear acoustics and its determination is of increasing interest in a number of areas ranging from underwater acoustics to medicine.

Thus, it is very transparent that the study of the properties of liquid state consists of a wide range of problems and to discuss all of them will certainly not be exhaustive but practically beyond the scope of the present work. In the present thesis, only some of the very important thermodynamical and thermoacoustical parameters of liquids and liquid mixtures have been investigated using different theories and relations. The theoretical results have compared with the available experimental data, and also non ideal nature of liquid mixtures have been assessed on the basis of different types of possible intermolecular interactions in the system.

Chapter 1 of the present thesis is introductory. It embodies the scope and outline of the present work. The various empirical, semi-empirical and statistical mechanical theories and approaches employed in present work are discussed in detailed and complete an up to date literature survey along with the background of the work is presented in this chapter.

Chapter 2 deals the computation of thermal conductivity of five binary mixtures of organic compounds namely DEG-DBE + n-dodecane, DEG-DME + n-dodecane, MEG-DME + n-dodecane, TEG-DME + n-dodecane and TRG-DME + n-dodecane at

298.15 K and 313.15 K. Sutherland Wassiljewa equation proposed for gases on the basis of uniform gaseous model have been used for the evaluation of thermal conductivity values of binary liquid mixtures. In addition to this Li's equation and several empirical relations proposed for viscosity of liquid mixtures are used for evaluation of thermal conductivity of aforementioned binary fluid mixtures. Theoretical results, thus obtained, have been compared with the experimental values, and it has been found that the agreement between both is found to be very good.

In chapter 3, evaluation of thermal conductivity values of six ternary fluid mixtures namely toluene + carbontetrachloride + chloroform, benzene + n-pentane + cyclohexane, benzene + chloroform + 2-propanol, toluene + benzene + n-pentane, cyclohexane + carbontetrachloride + 2-propanol, and n-pentane + toluene + 2-propanol have been carried out. Furthermore, Sutherland Wassiljewa equation and recently proposed Marcus relation⁹⁷ have been extended for multicomponent systems. In addition to above two methods, Flory theory is extended successfully for ternary systems under the present consideration. There is good agreement between experimental and theoretical values of thermal conductivity values. A comparative study has also been done

The aim of Chapter 4 is to develop of Flory theory for the description of thermodynamic behaviour of binary systems at high pressures. Recently extensive works on Flory theory has been done in substantial amount at zero pressure. In this section Flory theory has been developed for high pressure, and is used to evaluate various thermodynamic properties viz thermal expansion coefficient, isothermal compressibility, density, molar volume, ultrasonic velocity, adiabatic compressibility, internal pressure, Pseudo Grüneisen parameter, heat capacity at constant pressure, heat capacity at constant volume and specific heat capacity ratio of single binary mixture ($C_6H_5NO_2 + C_6H_6$) have been computed at various temperatures (293.15K, 303.15K and 313.15K) and elevated pressures (0.1Mpa, 5.0Mpa and 10Mpa) over entire composition range. Boanza *et al*¹⁻⁸ developed an equation of state for the evaluation of thermal expansion coefficient, isothermal compressibility, molar volume and density. Validity of these expressions have been tested and compared with the experimental

and theoretical values obtained by Flory theory. There is close agreement between experimental and theoretical values.

Chapter 5 deals thermodynamic behaviour of ternary liquid mixtures, which have been described using Flory statistical theory in its modified form. This theory was formulated for deducing various properties of multicomponent systems²² by considering equalization of two body interactions $X_{ij}=X_{ji}$. In the present work, it has been demonstrated that Flory theory shows better performance for various thermodynamic properties of ternary systems. If we consider all the interaction parameters ($X_{ij}, X_{ji}, X_{jk}, X_{kj}, X_{ik}, X_{ki}$) of ternary systems ij k . In earlier investigation²², it was assumed that $X_{ij}=X_{ji}, X_{jk}=X_{kj}, X_{ik}=X_{ki}$. Expressions all the six interaction parameters are deduced, and the values of molar volume, density, velocity, specific heat capacity at constant pressure specific heat capacity at constant volume, internal pressure, adiabatic compressibility, isothermal compressibility, thermal expansion coefficient, specific heat capacity ratio and Pseudo Gruneisen parameter of ternary systems namely, toluene (x_1) + n-heptane (x_2) + n-hexane (x_3), cyclohexane (x_1) + heptane (x_2) + n-hexane (x_3) and n-hexane(x_1) + heptane(x_2) + n-decane(x_3) at 298.15K have been computed. A close agreement between theoretical and experimental values shows the validity of present approach.

Chapter 6 deals with the thermo physical behaviour of metal alloys over a wide range of temperature. Equations of state predicted for metal alloys, are also helpful in describing thermodynamic properties. In the present work, we have employed Flory statistical theory to compute the thermodynamic properties of metal alloys namely K + Rb and Na + Cs at 323.15K, 423.15K and 523.15K over entire mole fraction range. Excellent agreement between theoretical and experimental values is observed.

Aim of chapter 7 is to study the interactions between the components of binary liquid mixtures using equation of state and various physical properties. In the present work refractive index, changes in refractive index (Δn) and molar refraction (ΔR), deviation in permittivity ($\Delta \epsilon$) and excess molar polarization (P^E) of six binary mixtures of 1,2-dichloroethane with n-heptane, n-decane, n-dodecane, n-tetradecane, n-hexadecane

and 2,2,4-trimethylpentane as second component have been computed at 293.15 K and 313.15 K and at different mole fractions using well established relations discussed in the theoretical section of this chapter. The values of isobaric thermal expansivity (α) of three binary mixtures, methyl acetoacetate + methanol, methylacetoacetate + ethanol and methylacetoacetate + hexanol have also been computed and compared with its experimental values. In order to evaluate refractive indices (n) of binary liquid mixtures, several equations have been used to test the validity of various mixing rules namely, Heller (He), Dale-Gladstone (D-G), Lorentz-Lorenz (L-L), Arago-Biot (A-B) Wiener (W), Eykman (Eyk), Oster (Os) equations.

Chapter 8 comprises the theoretical evaluation of acoustic non-linearity parameter (B/A) of binary and multicomponent systems using different approaches. In the present work, non-linearity parameter has been computed using thermodynamic method (modified Tong Dong equation), Hartmann method based on potential parameter and an empirical relation. A comparison of B/A values obtained from these methods has been made in order to review the above-mentioned approaches.

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CHAPTER-II

THEORETICAL EVALUATION OF THERMAL CONDUCTIVITY AND DIFFUSION COEFFICIENT OF BINARY LIQUID MIXTURES BASED ON GASEOUS MODELS AND EMPIRICAL RELATIONS

INTRODUCTION

Experimental data of thermal conductivity of gaseous mixtures (binary and higher order mixtures) have been analyzed on the basis of various models¹⁻⁴ using mathematical theories of non-uniform gases⁵. Very recently¹⁴ an attempt has been made to extend some of these gaseous state models for computing the thermal conductivity of few binary liquid mixtures. Due to scarcity of experimental data no further extension could be made on the theoretical estimation of thermal conductivity of liquid mixtures. Moreover, as far as our knowledge is concerned, it appears that such theoretical studies of diffusion coefficient have not been done due to the lack of experimental data. In the year 1999, accurate measurement of thermal conductivities of five binary liquid mixtures (DEG-DBE + n-dodecane (I), DEG-DME + n-dodecane (II), MEG-DME + n-dodecane (III), TEG-DME + n-dodecane (IV), TRG-DME + n-dodecane (V)) at 298.15K and 323.15K has been carried out by Burgdorf et. al.⁶. In the present work we are extending the theoretical methods for computing the thermal conductivities of the aforesaid binary liquid mixtures. For the computation of diffusion coefficient, we have employed the viscosity data of binary liquid mixtures for obtaining its values using recently (1999) proposed interrelation by Marcus⁷. In this way, theoretical values of diffusion coefficient are calculated for five binary liquid mixtures (2-(2-methoxy ethoxy)ethanol + propylenecarbonate(VI), carbontetra chloride + cyclohexane(VII), carbontetra chloride + benzene(VIII), cyclohexane + benzene(IX), n-heptane + n-toluene(X)) at 298.15K using the literature values of liquid viscosity and Marcus relation.

THEORETICAL

In the present work the Sutherland-Wassiljewa equation¹⁴ is applied to evaluate thermal conductivity and diffusion coefficient of binary liquid mixtures. The aforesaid equation for any transport property (say Z_m) can be expressed as,

$$Z_m = \frac{Z_1}{1 + A_{12} \frac{x_2}{x_1}} + \frac{Z_2}{1 + A_{21} \frac{x_1}{x_2}} \quad (1)$$

where Z_1 and Z_2 are the transport properties of the pure components 1 and 2. A_{12} and A_{21} are the Wassiljewa coefficients interpreted by Pandey *et al*^{3,4,8} and Grey *et al*^{1,2} as the ratio of efficiencies with which molecules '2' and '1' impede the transport of momentum by molecules '1'. x_1 and x_2 are the mole fractions of the first and second components of binary liquid mixtures.

Equation (1) was independently obtained by Sutherland (1895), Wassiljewa (1904) and Hirshfelder (1958) using quite different approaches. Sutherland expression was based on the predictions of simple kinetic theory whereas Wassiljewa derived it on the basis of mean free path. Hirschfelder approximation was based on Chapman and Enskog's kinetic theory. Sutherland-Wassiljewa, vide eq (1), is highly nonlinear and flexible, and capable of explaining even maxima or minima in any transport property-composition curve.

A new empirical form has been given to the Wassiljewa coefficient⁸, A_{ij} , to give the best possible results in the case of liquids. It is expressed as,

$$A_{ij} = \frac{1}{4} \left[1 + \left(\frac{Z_i}{Z_j} \right)^{\frac{1}{2}} \left(\frac{M_j}{M_i} \right)^{\frac{3}{8}} \right]^2 \quad (2)$$

where M_j and M_i represent molecular weights of components 'j' and 'i' respectively. Wilke¹⁵ proposed a modified expression for the coefficient which can be expressed as,

$$A_{ij} = \frac{1}{4} \left[1 + \left(\frac{Z_i}{Z_j} \right)^{\frac{1}{2}} \left(\frac{M_j}{M_i} \right)^{\frac{1}{4}} \right]^2 \left[\frac{2M_j}{M_i + M_j} \right]^{\frac{1}{2}} \quad (3)$$

Li⁴ proposed equation to predict thermal conductivity (λ) as follows:

$$\lambda_m = \sum_i \sum_j \phi_i \phi_j \lambda_{ij} \quad (4)$$

where

$$\lambda_{ij} = 2(\lambda_i^{-1} + \lambda_j^{-1})^{-1} \quad 4(a)$$

$$\phi_i = \frac{X_i V_i}{\sum X_i V_i} \quad 4(b)$$

$$\phi_j = 1 - \phi_i$$

Here Φ_i and Φ_j are the volume fractions of i^{th} and j^{th} components, V_i and V_j the molar volume of i^{th} and j^{th} components respectively.

Equation of Kendal and Monroe ⁹, which has no adjustable parameter, can be written as,

$$Z_m = \left[x_1 Z_1^{\frac{1}{3}} + x_2 Z_2^{\frac{1}{3}} \right]^3 \quad (5)$$

Hind *et al* ¹⁰ proposed the following equation:

$$Z_m = x_1^2 Z_1 + x_2^2 Z_2 + 2x_1 x_2 Z_{12} \quad (6)$$

Frenkel¹⁶, with the help of Eyring's model, developed the logarithmic relation for non -ideal binary liquid mixtures. It can be expressed as,

$$\log Z_m = x_1^2 \log Z_1 + x_2^2 \log Z_2 + 2x_1 x_2 \log Z_{12} \quad (7)$$

where

$$Z_{12} = \frac{Z_1 + Z_2}{2}$$

Above empirical relations, which have been used to compute viscosity are now applied to evaluate thermal conductivity and diffusion coefficient.

The self-diffusion coefficients were found to be strictly proportional to the fluidity of the liquids and to follow, at 298.15K, the simple relation ⁷

$$D\eta = (1.297 \pm 0.024) \times 10^{-12} \text{ m}^2 \text{ Pa} \quad (8)$$

Equation (8) has been used here to evaluate the diffusion coefficient (D) of pure components of liquid mixtures at 298.15K using literature values of viscosity (η) .

RESULTS AND DISCUSSION

Thermal conductivity (λ) of five different binary liquid mixtures of polyethers with n-dodecane [(DEG-DBE + n-dodecane (I), DEG-DME + n-dodecane (II), MEG-DME + n-dodecane (III), TEG-DME + n-dodecane (IV), TRG-DME + n-dodecane (V)] at 298.15 and 323.15K has been computed at different mole fractions using Wassiljewa equation with two different Wassiljewa coefficients and the empirical relations. First of all eq (2) and (3) is used to calculate Wassiljewa coefficients. In conjunction with these coefficients eq (1) have been used to compute thermal conductivity of aforementioned binary systems. The values of λ obtained with two different coefficients in conjunction with eq (1) are reported in column 3 and 4 of Table-1. Li proposed a relation to evaluate the thermal conductivity of binary and multicomponent systems which is given by eq (4). Required values in eq (4) are computed utilizing eqs (4a) and (4b). Results thus obtained by Li's equation are reported in column 5 of Table-1. Eqs (5), (6) and (7) are empirical in nature and were established by Kendal, Hind and Frenkel. These relations are used here to evaluate thermal conductivity of binary and multicomponent systems and are reported in columns 6, 7 and 8 of Table-1 respectively. The values thus obtained theoretically are compared with the experimental findings, and are found to be fairly in good agreement. Kendals empirical relation gives better results than others. Thermal conductivity increases with the size of dimethyl ethers. System (I) has smallest thermal conductivity. Simple one-parameter equations have justified the experimental data successfully⁶. Experimental results used for the comparative studies are discussed in terms of three body interactions and equation of state contributions to the mixing behavior. Thermal conductivity decreases with increase in temperature as depicted in Table-1. Required experimental data have been taken from the work of Burgdorf *et al* ⁶.

Diffusion coefficients (D) of five binary mixtures (2-(2-methoxyethoxy)ethanol + Propylencarbonate(I), carbonteterachloride + cyclohexane (II), carbonteterachloride + benzene (III), benzene + cyclohexane (IV) and n- heptane + toluene (V)) have been computed at different composition and at 298.15K. First of all eq (2) and (3) is used to calculate Wassiljewa coefficients. In conjunction with these coefficients eq (1) have been used to compute thermal conductivity of aforementioned binary systems. The values of λ obtained with two different coefficients in conjunction with eq (1) are reported in column 3 and 4 of Table-1. Equations (5), (6) and (7) are empirical in nature and were established by Kendal, Hind and Frenkel. These relations are used here to evaluate thermal conductivity of binary and multicomponent systems and are reported in columns 5, 6 and 7 of Table-1 respectively. A close perusal of Table-2 shows that the smallest and largest values of diffusion coefficients are obtained for system (I) and system (V) respectively. Diffusion coefficient evaluated in conjunction with eqs (1) and (3) predicts better results in most of the cases than others do. The close agreement between theoretical and experimental values indicates the success of the present approaches. Necessary data have been taken from earlier papers ¹¹⁻¹³.

Transport properties are of great importance because of well-established relationships between transport and thermodynamic properties⁷, and industrial applications of liquids. Still the thermodynamic relations permit the predictions of viscosities, their activation energy, self-diffusion coefficients and thermal conductivities of liquids at ambient conditions when certain generally available thermodynamic quantities of liquids are know

Table 1. Thermal conductivity of binary liquid mixtures at 298.15K and 323.15K in Watt/mK

DEG-DBE + n-dodecane at 298.15K

x_1	λ (exp)	λ eq (1)& (2)	λ eq (1)& (3)	λ eq (4)	λ eq (5)	λ eq (6)	λ eq (7)
0.093	0.1367	0.1368	0.1370	0.1368	0.1368	0.1368	0.1368
0.193	0.1365	0.1367	0.1380	0.1378	0.1377	0.1377	0.1377
0.311	0.1350	0.1388	0.1391	0.1388	0.1387	0.1387	0.1387
0.409	0.1353	0.1396	0.1400	0.1397	0.1395	0.1396	0.1395
0.494	0.1360	0.1404	0.1408	0.1404	0.1403	0.1403	0.1403
0.603	0.1368	0.1413	0.1417	0.1414	0.1412	0.1412	0.1412
0.702	0.1383	0.1422	0.1425	0.1422	0.1421	0.1421	0.1421
0.792	0.1392	0.1429	0.1432	0.1430	0.1429	0.1429	0.1429
0.903	0.1421	0.1439	0.1440	0.1439	0.1438	0.1439	0.1438

DEG-DME + n-dodecane at 298.15K

x_1	λ (exp)	λ eq (1)& (2)	λ eq (1)& (3)	λ eq (4)	λ eq (5)	λ eq (6)	λ eq (7)
0.093	0.1363	0.1373	0.1374	0.1370	0.1376	0.1377	0.1376
0.147	0.1359	0.1381	0.1382	0.1376	0.1385	0.1386	0.1385
0.296	0.1363	0.1404	0.1406	0.1395	0.1411	0.1413	0.1412
0.420	0.1380	0.1424	0.1427	0.1413	0.1433	0.1435	0.1433
0.512	0.1396	0.1440	0.1443	0.1428	0.1449	0.1451	0.1450
0.605	0.1393	0.1457	0.1460	0.1444	0.1466	0.1468	0.1466
0.707	0.1416	0.1476	0.1479	0.1465	0.1484	0.1486	0.1485
0.790	0.1462	0.1493	0.1495	0.1483	0.1499	0.1501	0.1500
0.903	0.1475	0.1517	0.1518	0.1511	0.1520	0.1521	0.1520

MEG-DME + n-dodecane at 298.15K

x_1	λ (exp)	λ eq (1)&(2)	λ eq (1)&(3)	λ eq(4)	λ eq(5)	λ eq(6)	λ eq(7)
0.129	0.1366	0.1367	0.1375	0.1368	0.1376	0.1376	0.1376
0.250	0.1358	0.1376	0.1390	0.1376	0.1391	0.1391	0.1391
0.410	0.1360	0.1390	0.1410	0.1389	0.1410	0.1411	0.1411
0.496	0.1367	0.1399	0.1421	0.1398	0.1421	0.1422	0.1421
0.628	0.1370	0.1416	0.1438	0.1413	0.1438	0.1439	0.1438
0.711	0.1395	0.1428	0.1449	0.1425	0.1448	0.1449	0.1448
0.799	0.1395	0.1443	0.1460	0.1439	0.1459	0.1460	0.1459
0.896	0.1424	0.1462	0.1472	0.1459	0.1472	0.1472	0.1472

TEG-DME + n-dodecane at 298.15K

x_1	λ (exp)	λ eq (1)&(2)	λ eq (1)&(3)	λ eq (4)	λ eq (5)	λ eq (6)	λ eq (7)
0.103	0.1371	0.1387	0.1389	0.1384	0.1385	0.1386	0.1385
0.203	0.3930	0.1412	0.1416	0.1407	0.1409	0.1412	0.1410
0.744	0.1508	0.1550	0.1554	0.1544	0.1547	0.1550	0.1548
0.803	0.1525	0.1565	0.1569	0.1560	0.1562	0.1565	0.1563
0.910	0.1571	0.1592	0.1594	0.1580	0.1591	0.1590	0.1591

TRG-DME + n-dodecane at 298.15K

x_1	λ (exp)	λ eq (1)&(2)	λ eq (1)&(3)	λ eq (4)	λ eq (5)	λ eq (6)	λ eq (7)
0.122	0.1367	0.1384	0.1384	0.1379	0.1384	0.1385	0.1384
0.215	0.1358	0.1402	0.1402	0.1394	0.1402	0.1404	0.1403
0.325	0.1393	0.1424	0.1424	0.1414	0.1424	0.1426	0.1425
0.410	0.1412	0.1441	0.1441	0.1429	0.1441	0.144	0.1442
0.514	0.1427	0.1462	0.1462	0.1450	0.1462	0.1465	0.1463
0.602	0.1440	0.1480	0.1480	0.1468	0.1481	0.1483	0.1481
0.699	0.1448	0.1500	0.1500	0.1489	0.1501	0.1503	0.1501
0.787	0.1497	0.1518	0.1519	0.1510	0.1519	0.1521	0.1519
0.899	0.1536	0.1542	0.1542	0.1530	0.1543	0.1543	0.1543

DEG-DBE + n-dodecane at 323.15K

x_1	λ (exp)	λ eq (1)&(2)	λ eq (1)&(3)	λ eq (4)	λ eq (5)	λ eq (6)	λ eq (7)
0.205	0.1305	0.1332	0.1335	0.1332	0.1331	0.1331	0.1331
0.310	0.1316	0.1343	0.1346	0.1343	0.1342	0.1342	0.1342
0.405	0.1329	0.1353	0.1357	0.1353	0.1351	0.1352	0.1352
0.502	0.1338	0.1363	0.1367	0.1363	0.1362	0.1362	0.1362
0.606	0.1343	0.1374	0.1377	0.1374	0.1372	0.1373	0.1373
0.703	0.1354	0.1384	0.1387	0.1384	0.1383	0.1383	0.1383
0.799	0.1359	0.1394	0.1396	0.1394	0.1393	0.1393	0.1393
0.909	0.1368	0.1405	0.1406	0.1405	0.1404	0.1405	0.1404

DEG-DME + n-dodecane at 323.15K

x_1	λ (exp)	λ eq (1)&(2)	λ eq (1)&(3)	λ eq (4)	λ eq (5)	λ eq (6)	λ eq (7)
0.060	0.1294	0.1318	0.1318	0.1316	0.1319	0.1320	0.1320
0.178	0.1288	0.1334	0.1335	0.1328	0.1338	0.1339	0.1338
0.247	0.1294	0.1343	0.1345	0.1336	0.1349	0.1350	0.1349
0.308	0.1297	0.1352	0.1354	0.1344	0.1359	0.1360	0.1359
0.404	0.1305	0.1367	0.1369	0.1357	0.1374	0.1376	0.1375
0.549	0.1325	0.1390	0.1392	0.1378	0.1398	0.1399	0.1398
0.619	0.1353	0.1401	0.1404	0.1390	0.1409	0.1411	0.1410
0.710	0.1364	0.1417	0.1420	0.1406	0.1424	0.1426	0.1425
0.800	0.1423	0.1434	0.1436	0.1425	0.1439	0.1440	0.1440
0.906	0.1423	0.1454	0.1455	0.1449	0.1457	0.1458	0.1457

MEG-DME + n-dodecane at 323.15K

x_1	λ (exp)	λ eq (1)&(2)	λ eq (1)&(3)	λ eq (4)	λ eq (5)	λ eq (6)	λ eq (7)
0.155	0.1293	0.1298	0.1307	0.1304	0.1299	0.1299	0.1299
0.302	0.1280	0.1286	0.1302	0.1298	0.1288	0.1288	0.1288
0.497	0.1288	0.1271	0.1292	0.1287	0.1274	0.1274	0.1274
0.730	0.1307	0.1255	0.1273	0.1270	0.1257	0.1257	0.1257
0.815	0.1340	0.1249	0.1264	0.1261	0.1251	0.1251	0.1251

TEG-DME + n-dodecane at 323.15K

x_1	λ (exp)	λ eq (1)&(2)	λ eq (1)&(3)	λ eq (4)	λ eq (5)	λ eq (6)	λ eq (7)
0.108	0.1297	0.1337	0.1384	0.1334	0.1335	0.1337	0.1336
0.209	0.1330	0.1362	0.1402	0.1357	0.1359	0.1362	0.1360
0.309	0.1341	0.1387	0.1424	0.1380	0.1383	0.1386	0.1384
0.395	0.1351	0.1408	0.1441	0.1401	0.1404	0.1408	0.1405
0.509	0.1400	0.1437	0.1462	0.1429	0.1432	0.1436	0.1433
0.607	0.1413	0.1461	0.1480	0.1453	0.1457	0.1460	0.1457
0.706	0.1434	0.1485	0.1500	0.1478	0.1481	0.1484	0.1482
0.805	0.1467	0.1509	0.1519	0.1504	0.1507	0.1509	0.1507
0.885	0.1500	0.1529	0.1542	0.1526	0.1527	0.1529	0.1528

TRG-DME + n-dodecane at 323.15K

x_1	λ (exp)	λ eq (1)&(2)	λ eq (1)&(3)	λ eq (4)	λ eq (5)	λ eq (6)	λ eq (7)
0.114	0.1291	0.1332	0.1332	0.1327	0.1332	0.1333	0.1332
0.193	0.1300	0.1347	0.1347	0.1340	0.1347	0.1349	0.1347
0.298	0.1313	0.1357	0.1367	0.1358	0.1368	0.1370	0.1368
0.404	0.1328	0.1388	0.1388	0.1377	0.1389	0.1391	0.1389
0.560	0.1365	0.1419	0.1419	0.1407	0.1420	0.1422	0.1420
0.702	0.1400	0.1448	0.1448	0.1437	0.1448	0.1450	0.1449
0.784	0.1410	0.1465	0.1465	0.1456	0.1465	0.1467	0.1466
0.895	0.1427	0.1488	0.1488	0.1483	0.1488	0.1489	0.1488

Table 2. Diffusion coefficient (D)(m^2s^{-1}) of binary liquid mixtures at 298.15K

2-(2-methoxy ethoxy)ethanol + propylenecarbonate at 298.15K

x_1	D (exp)	D eq (1)&(2)	D eq (1)&(3)	D eq (5)	D eq (6)	D eq (7)
0.034	5.1756	5.1369	5.1370	5.1480	5.1532	5.1496
0.063	5.1571	5.0823	5.0825	5.1019	5.1113	5.1047
0.085	5.1387	5.0424	5.0427	5.0679	5.0802	5.0715
0.110	5.1123	4.9966	4.9970	5.0284	5.0439	5.0329
0.141	5.0903	4.9421	4.9427	4.9809	4.9999	4.9864

0.162	5.0684	4.9051	4.9057	4.9482	4.9695	4.943
0.174	5.0506	4.8839	4.8846	4.9493	4.9519	4.9358
0.219	4.9865	4.8074	4.8082	4.8604	4.8872	4.8679
0.269	4.9036	4.7238	4.7247	4.7835	4.8143	4.7919
0.323	4.8073	4.6375	4.6385	4.70223	4.7363	4.7114
0.370	4.7146	4.5659	4.5670	4.6336	4.6699	4.6431
0.381	4.6806	4.5487	4.5498	4.6168	4.6537	4.6464
0.442	4.5605	4.4576	4.4588	4.5271	4.5655	4.5368
0.472	4.4941	4.4150	4.4163	4.4843	4.5231	4.4941
0.537	4.3670	4.3224	4.3237	4.3897	4.4283	4.3991
0.569	4.3075	4.2794	4.2806	4.3449	4.3829	4.3540
0.619	4.2344	4.2128	4.2140	4.2745	4.3110	4.2831
0.658	4.1731	4.1622	4.1633	4.2202	4.2550	4.2282
0.750	4.0317	4.0461	4.0470	4.0925	4.1214	4.0989
0.776	3.9932	4.0148	4.0157	4.0575	4.0842	4.0633
0.800	3.9676	3.9868	3.9876	4.0257	4.0504	4.0311
0.814	3.9519	3.9695	3.9706	4.0061	4.0293	4.0111
0.845	3.9149	3.9333	3.9340	3.9646	3.9847	3.9688
0.906	3.8521	3.8639	3.8644	3.8837	3.8968	3.8864
0.941	3.8102	3.8249	3.8252	3.8376	3.8460	3.8393
0.980	3.7791	3.7882	3.7829	3.7872	3.7901	3.7878

Corbontetrachloride + cyclohexane at 298.15K

x_1	D (exp)	D eq (1)&(2)	D eq (1)&(3)	D eq (5)	D eq (6)	D eq (7)
0.2753	14.5681	14.3795	14.5690	14.4670	14.4670	14.4670
0.3845	14.5469	14.3588	14.5701	14.4575	14.4575	14.4575
0.4727	14.5273	14.3500	14.5620	14.4498	14.4490	14.4490
0.5800	14.5030	14.3475	14.5030	14.4405	14.4405	14.4405
0.6707	14.3835	14.3515	14.5206	14.4326	14.4326	14.4326
0.7701	14.4609	14.3617	14.4905	14.4220	14.4240	14.4240
0.8640	14.4400	14.3760	14.4577	14.4158	14.4158	14.4158
0.6805	14.4819	14.3523	14.5179	14.4318	14.4318	14.4318
0.4418	14.5338	14.3524	14.5656	14.4525	14.4526	14.4526

corbontetrachloride + benzene at 298.15K

x_1	D (exp)	D eq (1)&(2)	D eq (1)&(3)	D eq (5)	D eq (6)	D eq (7)
0.137	20.2656	19.7780	19.9401	20.4064	20.5194	20.4000
0.181	19.8622	19.3054	19.5005	20.0648	20.2063	20.1059
0.218	19.5331	18.9384	19.1549	19.7840	19.9463	19.8303
0.252	19.3006	18.6126	18.4884	19.5224	19.7019	19.5727
0.288	19.0735	18.2903	18.5347	19.2512	19.4462	19.3049
0.319	18.8517	18.0310	18.2826	19.0233	19.2294	19.0792
0.471	17.6463	16.9030	17.1558	17.9142	18.1492	17.9730
0.615	16.7355	16.0442	16.2573	16.9094	17.1312	16.9608

cyclohexane + benzene at 298.15K

x_1	D (exp)	D eq (1)&(2)	D eq (1)&(3)	D eq (5)	D eq (6)	D eq (7)
0.2942	19.1298	18.9861	18.9822	19.2377	19.4296	19.2903
0.2613	19.3871	19.2435	19.2398	19.4811	19.6597	19.5309
0.2368	19.5038	19.4386	19.4351	19.6637	19.8311	19.7109
0.1692	19.6515	19.9926	19.9896	20.1734	20.3040	20.2115
0.1659	19.7412	20.0202	20.0173	20.1985	20.3271	20.2361
0.1226	19.8318	20.3883	20.3859	20.5299	20.6300	20.5598
0.0770	19.8318	20.7871	20.7854	20.8827	20.9490	20.9030
0.2951	19.2433	18.9791	18.9753	19.2310	19.4233	19.2837
0.6686	16.4803	16.3836	16.3807	16.6089	16.8104	16.6543

n-heptane + n-toluene at 298.15K

x_1	D (exp)	D eq (1)&(2)	D eq (1)&(3)	D eq (5)	D eq (6)	D eq (7)
0.6030	28.6998	28.1003	28.1237	28.3593	28.7920	28.4723
0.5790	28.3118	27.8008	27.8244	28.0612	28.5013	28.1745
0.5610	28.1040	27.5785	27.6021	27.8390	28.2833	27.9622
0.5500	27.9526	27.4435	27.4671	27.7038	28.1500	27.8168
0.5408	27.8625	27.3312	27.3547	27.5911	28.0386	27.7037
0.5328	27.7730	27.2739	27.2574	27.4933	27.9417	27.6056
0.5212	27.6546	27.0935	27.1169	27.3519	27.8012	27.4637
0.5171	27.5957	27.0536	27.0771	27.3117	27.7612	27.4234
0.5106	27.5372	26.9658	26.9892	27.2231	27.6728	27.3343
0.5045	27.4788	26.8926	26.9159	27.1492	27.5989	27.2600
0.4983	27.3918	26.8185	26.8417	27.0742	27.5238	27.1845
0.4953	27.3629	26.7827	26.8059	27.0380	27.4874	27.1481
0.4959	27.2471	26.7898	26.8130	27.0452	27.4947	27.1554
0.4771	27.1623	26.5665	26.5894	26.8188	27.2670	26.9274

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CHAPTER-III

THERMAL CONDUCTIVITY OF TERNARY LIQUID MIXTURES: APPLICATION OF FLORY'S EQUATION OF STATE AND UNIFORM GASEOUS MODEL

INTRODUCTION

Thermal conductivity of gaseous mixtures (binary and higher order) has been analyzed on the basis of various models¹⁻⁴ using mathematical theories of non-uniform gases⁵. Very recently⁶ an attempt has been made to extend some of these gaseous state models for computing the thermal conductivity of few binary mixtures. In the present communication, an extension of these gaseous states models has been made to evaluate the thermal conductivity of multicomponent liquid mixtures (toluene + carbontetrachloride + chloroform (I), benzene + n-pentane + cyclohexane (II), benzene + chloroform + 2-propanol (III), toluene + benzene + n-pentane (IV), cyclohexane + carbontetrachloride + 2-propanol (V), and n-pentane + toluene + 2-propanol (VI)). Moreover, Flory's statistical theory¹⁴⁻¹⁶ has also been used to predict thermodynamic properties of binary and multicomponent systems by various workers⁷⁻¹⁰ for which characteristics and reduced parameters of pure and multicomponent systems are required. Eyring and Marcus¹¹ have proposed relationships between thermal conductivity and various thermodynamic properties. In conjunction with the Flory statistical theory, these relations have been developed in terms of T , V , \bar{V} and modified expression for P^* to compute the thermal conductivity of ternary liquid mixtures. As far as our knowledge is concerned no such theoretical methods are available, so for, for the theoretical evaluation of thermal conductivity of multicomponent liquid systems.

THEORETICAL

Several empirical relations have been put forward for evaluating thermal conductivity of gaseous mixtures. In the present work, theoretically justified Sutherland-Wassiljewa equation⁴ is applied to evaluate the thermal conductivity of ternary liquid mixtures. The aforesaid equation for evaluating the thermal conductivity of multicomponent liquid mixtures can be expressed as,

$$\lambda = \sum_{i=1}^3 \lambda_i \left[1 + \sum_{j=1}^3 A_{ij} \frac{x_j}{x_i} \right]^{-1} \quad (1)$$

which in turn reduces for a ternary mixture

$$\lambda = \frac{\lambda_1}{1 + A_{12} \frac{x_2}{x_1} + A_{13} \frac{x_3}{x_1}} + \frac{\lambda_2}{1 + A_{23} \frac{x_3}{x_2} + A_{21} \frac{x_1}{x_2}} + \frac{\lambda_3}{1 + A_{31} \frac{x_1}{x_3} + A_{32} \frac{x_2}{x_3}} \quad (2)$$

where λ_1 , λ_2 and λ_3 are respectively the thermal conductivities of pure components 1, 2 and 3 of the ternary mixture.

Sutherland (1895), Wassiljewa (1904) and Hirschfelder¹² (1958) obtained eq (1) using quite different approaches. Sutherland expression was based on the predictions of kinetic theory of gases, whereas Wassiljewa derived it on the basis of mean free path. Hirschfelder approximation was based on Chapman and Enskog's kinetic theory. Sutherland-Wassiljewa equation is highly nonlinear and flexible, also capable of explaining even maxima or minima in any transport property composition curve.

A new empirical form has been proposed for Wassiljewa coefficient ⁶, A_{ij} , to give the best possible results in the case of liquids. It can be expressed as,

$$A_{ij} = \frac{1}{4} \left[1 + \left(\frac{\lambda_i}{\lambda_j} \right)^{\frac{1}{2}} \left(\frac{M_j}{M_i} \right)^{\frac{3}{8}} \right]^2 \quad (3)$$

where M_i and M_j represent molecular weights of components j and i respectively.

Flory *et al*¹⁴⁻¹⁶ introduced a parameter c to consider the van der Waals energy-volume relationship in cell partition function of Hirschfelder and Eyring. The reduced equation of state derived from resulting partition function is given by¹⁴

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3} - 1} - \frac{1}{\tilde{V}\tilde{T}} \quad (4)$$

where \tilde{P} , \tilde{V} and \tilde{T} are the reduced parameters of pressures, temperatures and volume of their respective pure components. Their numerical values can be obtained by using the following relations:

$$\tilde{P} = \frac{P}{P^*} = \frac{2PV^*}{S\eta} = \frac{P\beta_T}{\alpha T\tilde{V}} = \frac{P}{\gamma_P T\tilde{V}} \quad (5)$$

$$\tilde{T} = \frac{T}{T^*} = \frac{2V^*CRT}{S\eta} = \frac{\tilde{V}^{1/3} - 1}{\tilde{V}^{1/3}} \quad (6)$$

$$\tilde{V} = \frac{V}{V^*} = \left[\left(\frac{\alpha T}{3(1 + \alpha T)} \right) + 1 \right]^3 \quad (7)$$

The values of reduced and characteristic parameters obtained in this way are utilized in the resulting expression of excess volume of multicomponent systems. Considering all the possibilities of two body interactions and the statistical mechanical concept of Flory, intermolecular energy may be written as,

$$E_o = S_1 r_1 \eta_{11} + S_2 r_2 \eta_{22} + S_3 r_3 \eta_{33} - \frac{(\Delta \eta_1 A_{12} + \Delta \eta_2 A_{23} + \Delta \eta_3 A_{31})}{2V} \quad (8)$$

where

$$\Delta \eta_1 = \eta_{11} + \eta_{22} - 2\eta_{12} \quad (9a)$$

$$\Delta \eta_2 = \eta_{22} + \eta_{33} - 2\eta_{23} \quad (9b)$$

$$\Delta \eta_3 = \eta_{33} + \eta_{11} - 2\eta_{31} \quad (9c)$$

It will be assumed that random mixing of three components is taking place. Furthermore, site fraction can be written as,

$$\theta_3 = 1 - \theta_1 - \theta_2 = \frac{S_3 r_3 N_3}{S\bar{r}N} \quad (10a)$$

$$\theta_2 = 1 - \theta_1 - \theta_3 = \frac{S_2 r_2 N_2}{S\bar{r}N} \quad (10b)$$

On this basis

$$A_{12} = S_1 r_1 N_1 \theta_2 = S_2 r_2 N_2 \theta_3 \quad (11a)$$

$$A_{23} = S_2 r_2 N_2 \theta_3 = S_3 r_3 N_3 \theta_2 \quad (11b)$$

$$A_{31} = S_3 r_3 N_3 \theta_1 = S_1 r_1 N_1 \theta_3 \quad (11c)$$

where

$$\bar{r} = \frac{r_1 N_1 + r_2 N_2 + r_3 N_3}{N}$$

$$S = S_1 r_1 N_1 + S_2 r_2 N_2 + S_3 r_3 N_3$$

$$N = N_1 + N_2 + N_3$$

On substituting eqs (9) and (10) into eq (7), we get

$$-\frac{E_0}{\bar{r}N} = \frac{S}{2V} [\theta_1 \eta_{11} + \theta_2 \eta_{22} + \theta_3 \eta_{33} - \theta_1 \theta_2 \Delta \eta_1 - \theta_2 \theta_3 \Delta \eta_2 - \theta_3 \theta_1 \Delta \eta_3] \quad (12)$$

Defining the segment fractions,

$$\psi_3 = 1 - \psi_1 - \psi_2 = \frac{r_3 N_3}{\bar{r}N} \quad (13a)$$

$$\psi_2 = 1 - \psi_1 - \psi_3 = \frac{r_2 N_2}{\bar{r}N} \quad (13b)$$

we have

$$\frac{1}{\bar{r}} = \frac{\psi_1}{r_1} + \frac{\psi_2}{r_2} + \frac{\psi_3}{r_3} \quad (14)$$

$$S = \psi_1 S_1 + \psi_2 S_2 + \psi_3 S_3 \quad (15)$$

$$\theta_i = \sum \frac{\psi_i S_i}{S} \quad (16)$$

For the present systems, expressions for segment fraction and site fraction¹⁹ are given by

$$\psi_i = \frac{x_i V_i^*}{\sum x_i V_i^*}$$

and

$$\theta_i = \frac{\psi_i}{\psi_i + \sum_{k \neq i} \psi_k \left(\frac{V_i^*}{V_k^*} \right)^{1/3}}$$

The characteristic pressure of the pure component is given by

$$P_1^* = \frac{S_1 \eta_{11}}{2V^{*2}}, P_2^* = \frac{S_2 \eta_{22}}{2V^{*2}}, P_3^* = \frac{S_3 \eta_{33}}{2V^{*2}}$$

$$\eta_{11} = \frac{2P_1^* V^{*2}}{S_1}, \eta_{22} = \frac{2P_2^* V^{*2}}{S_2}, \eta_{33} = \frac{2P_3^* V^{*2}}{S_3},$$

By analogy, we define

$$X_{12} = \frac{S_1 \Delta \eta_1}{2V^{*2}}, X_{23} = \frac{S_2 \Delta \eta_2}{2V^{*2}}, X_{31} = \frac{S_3 \Delta \eta_3}{2V^{*2}}$$

$$X_{21} = \frac{S_2 \Delta \eta_2}{2V^{*2}}, X_{32} = \frac{S_3 \Delta \eta_3}{2V^{*2}}, X_{13} = \frac{S_1 \Delta \eta_1}{2V^{*2}}$$

Using these expressions, we can find,

$$\Delta \eta_1 = \frac{(X_{12} + X_{13})V^{*2}}{S_1}, \Delta \eta_2 = \frac{(X_{23} + X_{21})V^{*2}}{S_2}, \Delta \eta_3 = \frac{(X_{31} + X_{32})V^{*2}}{S_3}, \quad (17)$$

From eqs (16), (17) and (11), we get

$$-\frac{E_0}{\bar{F}N} = \frac{S}{2V} \left[\theta_1 \frac{2P_1^* V^{*2}}{S_1} + \theta_2 \frac{2P_2^* V^{*2}}{S_2} + \theta_3 \frac{2P_3^* V^{*2}}{S_3} - \frac{\theta_1 \theta_2 (X_{12} + X_{13})V^{*2}}{S_1} - \frac{\theta_2 \theta_3 (X_{23} + X_{21})V^{*2}}{S_2} - \frac{\theta_3 \theta_1 (X_{31} + X_{32})V^{*2}}{S_3} \right]$$

On simplification, one gets,

$$-\frac{E_0}{\bar{F}N} = \frac{V^{*2}}{V} \left[\psi_1 P_1^* + \psi_2 P_2^* + \psi_3 P_3^* - \psi_1 \theta_2 \left(\frac{X_{12} + X_{13}}{2} \right) - \psi_1 \theta_3 \left(\frac{X_{12} + X_{13}}{2} \right) - \psi_1 \theta_2 \left(\frac{X_{12} + X_{13}}{2} \right) \right] \quad (18)$$

By analogy with the energy for a pure component, we define

$$-\frac{E_0}{\bar{F}N} = \frac{P^* V^*}{\bar{V}} = \frac{CKT^*}{\bar{V}} \quad (19)$$

Comparing eqs (18) and (19)

$$P^* = \psi_1 P_1^* + \psi_2 P_2^* + \psi_3 P_3^* - \psi_1 \theta_2 \left(\frac{X_{12} + X_{13}}{2} \right) - \psi_2 \theta_3 \left(\frac{X_{23} + X_{21}}{2} \right) - \psi_3 \theta_1 \left(\frac{X_{31} + X_{32}}{2} \right) \quad (20)$$

which is the modified expression for the characteristic pressure for a ternary liquid mixtures as developed in the present work. In the case of multicomponent system, interaction parameter is defined as,²⁰

$$X_{i,j} = P_i^* \left[1 - \left(\frac{P_i^*}{P_i^*} \right)^{1/2} \left(\frac{V_i^*}{V_i^*} \right)^{1/6} \right]^2 \quad (21)$$

and the characteristic temperatures is given by^{19,20}

$$T^* = \frac{P^*}{\sum_{i=1}^3 \frac{\psi_i P_i^*}{T_i^*}} \quad (22)$$

The reduced temperature

$$\tilde{T} = \frac{T}{T^*} \quad (23)$$

Ideal reduced volume and the ideal reduced temperature for a multicomponent system are expressed as,¹⁶

$$\tilde{V}^0 = \sum_{i=1}^3 X_i \tilde{V}_i \quad (24)$$

$$\tilde{T}^0 = \frac{\tilde{V}^{0^{1/3}} - 1}{\tilde{V}^{0^{1/3}}} \quad (25)$$

The excess reduced volume is given by^{16,20}

$$\tilde{V}^E = \tilde{V}^{0^{2/3}} \left(\frac{4}{3} - \tilde{V}^{0^{1/3}} \right)^{-1} (\tilde{T} - \tilde{T}^0) \quad (26)$$

The reduced volume for the mixture can be expressed as,

$$\tilde{V} = \tilde{V}^E + \tilde{V}^0 \quad (27a)$$

$$V^* = \frac{V}{\tilde{V}} \quad (27b)$$

Assuming contribution of translational and rotational degrees of freedom in the transference of energy, Eyring¹² proposed an expression for evaluating thermal conductivity of liquids which is given by

$$\lambda = 2.8 k n^{2/3} \gamma^{-1/2} c \quad (28)$$

where k is the Boltzmann constant, n the number of molecules per unit volume, γ is the heat capacity ratio and c is ultrasonic velocity. For multicomponent systems, eq (28) can be expressed in terms of characteristic and reduced parameters obtained from the Flory's statistical theory given as follows:

$$\lambda = 2.8k \left(\sum_i n_i \phi_i \right)^{2/3} \left[\frac{P^* V^* \left[1 - 3 \left(\tilde{V}^{1/3} - 1 \right) \right]}{3 \tilde{V} \left(\sum_i X_i M_i \right) \left(\tilde{V}^{1/3} - 1 \right)} \right]^{1/2} \quad (29)$$

In the year 1999, Marcus¹¹ proposed several relationships between transport properties and thermodynamic properties. Assuming significant contribution of potential energy term than kinetic energy, he proposed expression for the thermal conductivity as a function of thermodynamic properties, which can be expressed as,

$$\lambda / W m^{-1} K^{-1} = 0.0695 \left[\left(\frac{C_p}{V} \right) / (cm^3 J^{-1} K^{-1}) \right] + (0.00205) \left(\frac{M}{kgmol} \right)^{-1} \quad (30)$$

In terms of characteristic pressure, characteristic temperatures and reduced volume, above-mentioned equation can be written as,

$$\lambda / W m^{-1} K^{-1} = \frac{0.0695 \left[\frac{1}{V^* \tilde{V}} \left\{ \sum_i X_i C_p + \frac{P^* V^*}{T^*} \left[\frac{1}{\left(\frac{4}{3} \tilde{V}^{1/3} - 1 \right)} - \sum \left(\frac{X_i}{\left(\frac{4}{3} \tilde{V}_i^{1/3} - 1 \right)} \right) \right] \right\} \right]}{cm^3 J^{-1} K^{-1}} + 0.00205 \left(\frac{X_i M_i}{kgmol} \right)^{-1} \quad \dots \quad (31)$$

RESULTS AND DISCUSSION

In the present work thermal conductivities of six ternary liquid systems; namely toluene + carbontetrachloride + chloroform (I), benzene + n-pentane + cyclohexane (II), benzene + chloroform + 2-propanol (III), toluene + benzene + n-pentane (IV), cyclohexane + carbontetrachloride + 2-propanol (V) and n-pentane + toluene + 2-propanol (VI) have been computed at 298.15 K and ambient pressures, and entire range of mole fractions using Wassiljewa equation, vide eqs (29) and (31). The experimental data needed for thermal conductivity of pure components have been taken from earlier papers^{13,18}.

Various workers^{3,4,6} have applied Wassiljewa equation to study the transport properties of binary and multicomponent systems of gases. In the present work an extension of this equation to ternary liquid mixtures for computing the thermal conductivities has been done. Various interaction parameters A_{12} , A_{21} , A_{13} , A_{31} , A_{23} and A_{32} have been evaluated using eq (2). Thermal conductivities of pure components and previously mentioned interaction parameters have been utilized to compute the thermal conductivities of aforementioned ternary systems with the Sutherland-Wassiljewa approach given by eq (1), which is completely based on non-uniform gaseous models. Results, thus obtained, are in close agreement with maximum and minimum APD of 5.35% and 1.28% for systems (I) and (VI) respectively as reported in column 4 of Table-1. Order of average percentage deviation for six ternary systems under investigation with Wassiljewa equation has following sequence:

System I > System V > System II > System III > System IV > System VI.

In liquid mixtures interactions are stronger in comparison to gases. Due to lack of considerations of these interactions in the Wassiljewa equation there is considerable difference between the theoretical and experimental values of thermal conductivities.

Flory's statistical theory¹⁴⁻¹⁶ has also been employed to compute the thermodynamic properties of binary and multicomponent systems by various workers^{7-10, 17}. Characteristic and reduced parameters of pure components are evaluated by the

procedure adopted by Pandey et al.^{7, 21}. Characteristic and reduced parameters of ternary liquid mixtures have been computed utilizing eqs (20), (22), (23) and (27).

A relationship between thermal conductivity, ultrasonic velocity and heat capacity ratio, based on Eyring assumptions where only the rotational and translational degrees of freedom are assumed to be effective in transferring energy, can be expressed in terms of characteristic pressure, characteristic volume and reduced volume of ternary liquid system, and is given by eq (29). This equation applies well for large number of liquids. Equation (29) in conjunction with eqs (20), (22), (23) and (27) have been used to compute thermal conductivity of all the ternary systems under the present investigation. With the reference of this equation, theoretical values of thermal conductivity show maximum and minimum APD of 12.24% and 2.67% for system III and system VI respectively as reported in column 5 of Table-1. However trend of APD for all the six ternary systems is given as follows:

System III > System V > System I > System II > System IV > System VI.

Very recently the proposed relationship between thermal conductivity and specific heat capacity at constant pressure, molar volume and molecular weight by Marcus has been also employed to evaluate the thermal conductivities of ternary liquid systems at 298.15K. To proceed this approach, Marcus relation has been expressed in terms of characteristic and reduced parameters utilizing eqs (30), (20), (22), (23) and (27). On simplification we get eq (31), which is used to compute the thermal conductivities of aforementioned ternary systems. Maximum and minimum deviations (APD) in their values is 16.03% and 3.63% for system V and system IV respectively as reported in column 6 of Table-1. Relative merits of the validity for the various ternary liquid systems are as follows:

System V > System VI > System III > System I > System II > System IV.

Maximum deviations are observed at higher concentrations of 2- propanol in ternary systems. This is due to intermolecular hydrogen bonding where interaction is much stronger. These interactions have not been considered in Flory theory in the evaluation of reduced and characteristic parameters.

Table 1. Thermal conductivity of ternary liquid mixtures (in mW/(m-K)) at 298.15K

toluene (x_1) + carbontetrachloride (x_2) + chloroform (x_3)					
x_1	x_2	λ (exp)	λ eq (2)	λ eq (29)	λ eq (31)
0.6864	0.1370	116.16	121.56	127.42	122.71
0.2802	0.5035	102.98	108.96	112.29	116.74
0.2555	0.1530	108.20	113.34	119.93	126.57
0.5038	0.3018	108.99	115.24	119.23	119.66
0.4828	0.1446	111.77	117.43	122.49	123.99
0.2673	0.3202	105.73	111.15	115.12	121.44
0.4177	0.2502	107.76	114.57	118.30	121.61
		APD	-5.35%	-9.60%	-12.06%

benzene (x_1) + n-pentane (x_2) + cyclohexane (x_3)					
x_1	x_2	λ (exp)	λ eq (2)	λ eq (29)	λ eq (31)
0.5987	0.2161	125.33	130.81	137.49	131.41
0.1932	0.6275	117.51	119.07	117.96	134.04
0.2055	0.2224	118.01	122.37	129.17	129.31
0.3927	0.4251	121.39	124.73	128.03	133.99
0.4050	0.2192	120.83	126.53	133.56	132.19
0.1991	0.4312	112.42	120.68	123.67	133.10
0.3291	0.3563	118.22	123.90	128.51	134.05
		APD	-4.15%	-7.75%	-11.44%

benzene (x_1) + chloroform (x_2) + 2-propanol (x_3)					
x_1	x_2	λ (exp)	λ eq (2)	λ eq (29)	λ eq (31)
0.6056	0.1321	131.73	135.11	145.60	138.80
0.2846	0.4605	118.34	123.38	134.10	141.49
0.1801	0.1178	131.22	133.42	148.48	157.88
0.4340	0.2840	125.89	129.25	139.97	139.75
0.3837	0.1245	131.98	134.21	146.90	147.42
0.2038	0.2666	124.13	128.43	140.91	149.59
0.3341	0.2186	126.64	130.70	142.70	145.71
		APD	-2.79%	-12.24%	-14.79%

toluene (x_1) + benzene (x_2) + n-pentane (x_3)

x_1	x_2	λ (exp)	λ eq (2)	λ eq (29)	λ eq (31)
0.5498	0.2162	126.21	129.31	133.54	127.86
0.1719	0.6085	130.09	133.26	136.81	131.17
0.1664	0.1962	118.18	121.12	118.62	134.17
0.3548	0.4186	128.43	131.28	135.44	129.29
0.3488	0.2057	123.02	125.02	126.36	130.89
0.1691	0.3990	123.82	126.96	127.35	132.82
0.2861	0.3375	124.87	127.53	129.46	131.04
		APD	-2.27%	-3.61%	-4.98%

cyclohexane (x_1) + carbontetrachloride (x_2) + 2-propanol (x_3)

x_1	x_2	λ (exp)	λ eq (2)	λ eq (29)	λ eq (31)
0.6064	0.1106	115.72	120.07	129.49	127.98
0.2474	0.4061	105.28	112.21	116.88	122.79
0.1740	0.0952	122.46	127.70	129.86	148.08
0.4450	0.2435	110.15	116.19	123.10	125.34
0.3740	0.1023	118.49	123.87	135.04	136.76
0.2043	0.2236	113.79	120.04	128.09	134.98
0.3345	0.1830	113.99	120.24	129.02	132.51
		APD	-5.09%	-11.49%	-16.03%

n-pentane (x_1) + toluene (x_2) + 2-propanol (x_3)

x_1	x_2	λ (exp)	λ eq (2)	λ eq (29)	λ eq (31)
0.6020	0.1571	119.77	121.37	116.51	142.06
0.2198	0.5163	128.22	129.05	131.73	137.66
0.1857	0.1454	131.32	132.43	139.89	156.83
0.4196	0.3286	123.09	125.04	122.70	139.86
0.3858	0.1510	124.43	126.83	125.74	148.10
0.2013	0.3153	129.92	130.73	134.97	146.76
0.3311	0.2593	125.26	127.62	126.93	144.86
		APD	-1.28%	-2.67%	-15.25%

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CHAPTER-IV

**THERMODYNAMIC BEHAVIOR OF
BINARY LIQUID MIXTURES AT
ELEVATED PRESSURES AND
VARYING TEMPERATURES:
APPLICATION OF FLORY'S
STATISTICAL THEORY AND THE
EQUATION OF STATE APPLIED AT
HIGH PRESSURES**

INTRODUCTION

Thermodynamic behaviour of binary and multicomponent systems is of considerable interest. Keeping this view in mind, measurements of few thermodynamic properties have been done at substantial amount^{1,2}. In addition to the experimental measurements, theoretical predictions of thermodynamic properties of pure, binary and multicomponent systems have also been done at normal temperature and pressure³⁻¹¹. Recently, Flory's statistical theory¹⁻¹¹, significant structure theory²², some other theories²³⁻²⁵, models²⁶⁻²⁸ and empirical³⁷⁻³⁹ relations have been widely used to describe the thermodynamic behavior of binary and multicomponent systems at normal pressure and varying temperatures. In the year 1980 Takagi and his coworkers²⁹⁻³⁶ carried out accurate measurements of density and velocity at elevated pressures. No attempt has yet been made to discuss the physico-chemico behavior of liquid mixtures at elevated pressures theoretically due to lack of experimental data. Theoretical predictions of thermal expansion coefficient, isothermal compressibility, density and molar volume of binary and multicomponent systems at high pressures have been made by Boanza *et al.*¹⁵⁻²¹. In present work, Flory's statistical theory has been successfully applied to estimate the thermodynamic properties of binary liquid mixtures at elevated pressures. For such study reduced equation of state derived by Flory has been used without assuming zero pressure as done in recent work¹⁻¹¹. Theoretical results, thus obtained have been compared with the experimental findings and with those obtained by equation of Boanza *et al.*^{15,16}. Results are found to be quite satisfactorily.

THEORETICAL

The reduced partition function, as obtained by Flory, can be written as¹²⁻¹⁴,

$$Z = Z_{comb} \left[\gamma (\bar{V}^*)^{r_{Nc}} \left(\bar{V}^{\frac{1}{3}} - 1 \right) \right]^{3r_{Nc}} \exp \left(\frac{r_{NC}}{\bar{V}T} \right) \quad (1)$$

which yields the reduced equation of state

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{\frac{1}{3}}}{\left(\tilde{V}^{\frac{1}{3}} - 1\right)} - \frac{1}{\tilde{V}T} \quad (2)$$

where C is the parameter introduced by Prigogine for the mean number of external degrees of freedom per segment. Equation (2) can be simplified to obtain the expression for reduced temperature, which is given as follows:

$$\tilde{T} = \tilde{P}\tilde{V} + \tilde{V}^{-1} - \tilde{P}\tilde{V}^{\frac{2}{3}} - \tilde{V}^{-\frac{4}{3}} \quad (3)$$

The reduced parameters are given by

$$\tilde{V} = \frac{V}{V^*} \quad (4)$$

$$\tilde{T} = \frac{T}{T^*} = \frac{2V^*CRT}{s\eta} \quad (5)$$

$$\tilde{P} = \frac{P}{P^*} = \frac{2PV^{*2}}{s\eta} \quad (6)$$

The coefficient of thermal expansion, the coefficient of isothermal compressibility and thermal pressure coefficient may be expressed in terms of reduced variables as,

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\tilde{T}}{T\tilde{V}} \right) \left(\frac{\partial \tilde{V}}{\partial \tilde{T}} \right)_{\tilde{P}} \quad (7)$$

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = - \left(\frac{\tilde{P}}{P\tilde{V}} \right) \left(\frac{\partial \tilde{V}}{\partial \tilde{P}} \right)_{\tilde{T}} \quad (8)$$

$$\gamma_P = \left(\frac{\partial P}{\partial T} \right)_V = \frac{\alpha}{\beta_T} = \left(\frac{\tilde{T}P}{T\tilde{P}} \right) \left(\frac{\partial \tilde{P}}{\partial \tilde{T}} \right)_{\tilde{V}} \quad (9)$$

Using required partial derivatives and reduced parameter obtained from eq (2), eqs (7), (8) and (9) can be written as,

$$(\alpha T)^{-1} = \left[\frac{1}{3 \left(\tilde{V}^{\frac{1}{3}} - 1 \right)} - 1 + \frac{2\tilde{P}\tilde{V}^2}{\left(\tilde{P}\tilde{V}^2 + 1 \right)} \right] \quad (10)$$

$$(\beta_T P)^{-1} = \left[\frac{1}{3 \left(\tilde{V}^{\frac{1}{3}} - 1 \right)} - 1 \right] \left[1 + \frac{1}{\tilde{P}\tilde{V}^2} \right] + 2 \quad (11)$$

$$\frac{\gamma T}{P} = 1 + \frac{1}{\tilde{P}\tilde{V}^2} \quad (12)$$

Reduced parameters \tilde{P} and \tilde{V} can be expressed in different form as follows:

Case I: When P, T, γ and β_T are known

$$\tilde{P} = \frac{P}{(\gamma T - P)} \frac{1}{\left[1 + \frac{\gamma T \beta_T}{3(1 - 2P\beta_T + \gamma T \beta_T)} \right]^6} \quad (13)$$

$$\tilde{V} = \left[1 + \frac{\gamma T \beta_T}{3(1 - 2P\beta_T + \gamma T \beta_T)} \right]^3 \quad (14)$$

Case II : When P, T, γ and α are known

$$\tilde{P} = \frac{P}{(\gamma T - P)} \frac{1}{\left[1 + \frac{\gamma T \alpha}{3(\gamma - 2P\alpha + \gamma T \alpha)} \right]^6} \quad (15)$$

$$\tilde{V} = \left[1 + \frac{\gamma T \alpha}{3(\gamma - 2P\alpha + \gamma T \alpha)} \right]^3 \quad (16)$$

Case III: When P, T, α and β_T are known

$$\tilde{P} = \frac{\beta_T P}{(\alpha T - \beta_T P)} \frac{1}{\left[1 + \frac{\alpha T}{3(1 - 2\beta_T P + \alpha T)} \right]^6} \quad (17)$$

$$\tilde{V} = \left[1 + \frac{\alpha T}{3(1 - 2\beta_T P + \alpha T)} \right]^3 \quad (18)$$

With the help of eqs (3), (4), (5), (6) and (13), (14) or (15), (16) or (17), (18) reduced (\tilde{P} , \tilde{V} and \tilde{T}) and characteristic (P^* , V^* and T^*) parameters of pure components can be calculated. These parameters for binary liquid mixtures have been computed using following expressions:

$$P^* = [\psi_1 P_1^* + \psi_2 P_2^* - \psi_1 \theta_2 X_{12}] \quad (19)$$

In the extension of Flory theory, Pandey and Pant¹⁰ defined an element (or segment) as an arbitrary chosen portion of the molecule, and again defined the segment as well as site fraction of molecules by the following relations¹⁰:

$$\psi_i = \frac{x_i V_i^*}{\sum x_i V_i^*} \quad (20a)$$

and

$$\theta_i = \frac{\psi_i}{\psi_i + \sum_{k \neq i} \psi_k \left(\frac{V_i^*}{V_k^*} \right)^{1/3}} \quad (20b)$$

In the case of multicomponent system, interaction parameter is defined as¹¹,

$$X_{ij} = P_i^* \left[1 - \left(\frac{P_j^*}{P_i^*} \right)^{1/2} \left(\frac{V_j^*}{V_i^*} \right)^{1/6} \right]^2$$

The characteristic temperatures and reduced temperature are given by^{10,11}

$$T^* = \frac{P^*}{\sum_{i=1}^3 \frac{\psi_i P_i^*}{T_i^*}} \quad (21)$$

and

$$\tilde{T} = \frac{T}{T^*} \quad (22)$$

Ideal reduced volume and the ideal reduced temperature for a multicomponent system are expressed as,

$$\tilde{V}^0 = \sum_{i=1}^3 X_i \tilde{V}_i \quad (23)$$

$$\tilde{T}^0 = \tilde{P} \tilde{V}^0 + \tilde{V}^{0-1} - \tilde{P} \tilde{V}^{0\frac{2}{3}} - \tilde{V}^{0-\frac{4}{3}} \quad (24)$$

The excess reduced volume is given by

$$\tilde{V}^E = \frac{(\tilde{T} - \tilde{T}^0)}{\left[\tilde{P} - \tilde{V}^{-2} - \frac{2}{3} \tilde{P} \tilde{V}^{-\frac{1}{3}} + \frac{4}{3} \tilde{V}^{-\frac{7}{3}} \right]} \quad (25)$$

The reduced volume for the mixtures is given by

$$\tilde{V} = \tilde{V}^E + \tilde{V}^0 \quad (26a)$$

$$V^* = \frac{V}{\tilde{V}}$$

Or

$$V = V^* \tilde{V}$$

Or

$$V = \left(\sum x_i V_i^* \right) \tilde{V} \quad (26b)$$

The excess volume of the mixture is defined as,

$$V^E = \left(\sum x_i V_i \right) \tilde{V}^E \quad (27)$$

Thermal expansion coefficient of the mixtures is calculated by the equation

$$\alpha = \frac{1}{T \left[\frac{1}{3 \left(\tilde{V}^{\frac{1}{3}} - 1 \right)} - 1 + \frac{2 \tilde{P} \tilde{V}^2}{\tilde{P} \tilde{V}^2 + 1} \right]} \quad (28)$$

Isothermal compressibility for liquid mixtures can be computed using the following expression:

$$\beta_T = \frac{1}{P \left[\left\{ \frac{1}{3 \left(\tilde{V}^{\frac{1}{3}} - 1 \right)} - 1 \right\} \left\{ 1 + \frac{1}{\tilde{P} \tilde{V}^2} \right\} + 2 \right]} \quad (29)$$

Internal pressure (P_i) can be expressed as a function of thermal expansion coefficient, α , and isothermal compressibility, β_T , through the relation

$$P_i = \frac{\alpha T}{\beta_r} - P \quad (30)$$

To compute heat capacity at constant pressure and excess heat capacity, following expressions have been used:

Heat capacity at constant pressure of mixtures (C_p) is given by

$$C_p = C_p^E + C_{p(idl)} \quad (31)$$

where $C_{p(idl)}$ is the ideal heat capacity of mixture

$$C_{p(idl)} = \sum x_i C_{pi} \quad (32)$$

C_{pi} = Heat capacity of i^{th} pure component.

Expression for C_p^E given by Khanwalkar *et al*⁸ for zero pressure is modified in the present work for its applicability at high pressures. The resulting expression is

$$C_p^E = \frac{P^* V^*}{T^*} \left[\frac{1}{\left(\tilde{P} \tilde{V}^2 - \frac{2}{3} \tilde{P} \tilde{V}^{\frac{5}{3}} + \frac{4}{3} \tilde{V}^{\frac{1}{3}} - 1 \right)} - \sum_i \left[\frac{x_i}{\left(\tilde{P}_i \tilde{V}_i^2 - \frac{2}{3} \tilde{P}_i \tilde{V}_i^{\frac{5}{3}} + \left(\frac{4}{3} \tilde{V}_i^{\frac{1}{3}} - 1 \right) \right)} \right] \right] \quad (33)$$

Adiabatic compressibility has been evaluated utilizing the well-known thermodynamic relation

$$\beta_r - \beta_s = \frac{\alpha^2 T V}{C_p} \quad (34)$$

which in turn becomes

$$\beta_s = \beta_r - \frac{\alpha^2 T V}{C_p} \quad (35)$$

With the help of eq (32), β_s for the mixtures can be calculated.

The specific heat ratio (γ) and specific heat capacity at constant volume for the mixture can be calculated using the following relation:

$$\gamma = \frac{\beta_r}{\beta_s} = \frac{C_p}{C_v} \quad (36)$$

Pseudo-Gruneisen parameter (Γ) of the mixture has been evaluated using the following relation:

$$\Gamma = \frac{\gamma - 1}{\alpha T} \quad (37)$$

For the evaluation of density of mixture following simplifying expression has been taken into account

$$\rho = \frac{M}{V} \quad (38)$$

Or

$$\rho = \frac{\sum x_i M_i}{\left(\sum x_i V_i^* \right) \tilde{V}} \quad (39)$$

Ultrasonic velocity in the mixture has been obtained with the help of following thermodynamic expression:

$$c = \left(\frac{1}{\beta_s \rho} \right)^{\frac{1}{2}} \quad (40)$$

Equation of states based on Pseudo spinodal hypothesis, which states that there exists a limit of mechanical stability of the liquid where the thermodynamic properties of the liquid diverge. According to which, the thermal expansion coefficient, α_p , the isothermal compressibility, β_T , density, ρ , and molar volume, V , can be expressed in the following form along a given isotherm as a function of the pressure $P^{15,16}$:

$$\alpha_p(P) = \alpha^* (P - P_s)^{-\gamma'} \quad (41)$$

$$\beta_T(P) = \beta_T^* (P - P_s)^{-\gamma} \quad (42)$$

$$\rho(P) = \rho_s \exp \left\{ \left[\frac{\beta_T^*}{1 - \gamma} \right] (P - P_s)^{(1-\gamma)} \right\} \quad (43)$$

$$V(P) = V_{sp} \exp \left\{ - \left[\frac{\beta_T^*}{1 - \gamma} \right] (P - P_s)^{(1-\gamma)} \right\} \quad (44)$$

where α^* and β_T^* are proportionality constants, γ and γ' the pseudocritical exponents, which characterize the divergence of each quantity, and P_s is the divergence pressure at the pseudospinodal curve. While α^* , β_T^* and P_s are functions of temperature, the pseudocritical exponents are assumed to be universal constants of value $\gamma'=0.50$ and $\gamma=0.85$.

If eq(42) holds, two values of β_T , measured at two different pressures along a given isotherm, allow us to determine the two characteristic parameter β_T^* and P_s at this temperature. Moreover eqs (41) to (44) have been extended to mixtures by Baonza *et al*¹⁵.

Thermal expansion coefficient and isothermal compressibility of binary liquid mixture can be expressed as^{40, 41},

$$\alpha = \frac{75.6 \times 10^{-3}}{T^{\frac{1}{9}} c^{\frac{3}{2}} \rho^{\frac{1}{3}}} \quad (45)$$

and

$$\beta_T = \frac{1.71 \times 10^{-3}}{T^{\frac{4}{9}} c^{\frac{1}{2}} \rho^{\frac{4}{3}}} \quad (46)$$

In conjunction with eqs (45) and (46), eq (30) becomes

$$P_{\text{int}} = 44.2 T^{\frac{4}{3}} c^{\frac{3}{2}} \rho - P \quad (47)$$

RESULTS AND DISCUSSION

Thermal expansion coefficient, isothermal compressibility, density, molar volume, ultrasonic velocity, adiabatic compressibility, internal pressure, Pseudo-Grüneisen parameter, heat capacity at constant pressure, heat capacity at constant volume and specific heat capacities ratio of single binary mixture ($C_6H_5NO_2 + C_6H_6$) have been computed at various temperatures (293.15K, 303.15K and 313.15K) and elevated pressures (0.1Mpa, 5.0Mpa and 10Mpa) in the entire composition range. Experimental data of pure components and binary mixtures have been taken from the paper of Takagi and Teranishi²⁹. Flory's statistical theory has been employed to compute the thermodynamic properties of binary liquid mixture at aforementioned temperatures and pressures. Moreover, equations of state developed by Baonza *et al*^{15,16} has been used here to compute thermal expansion coefficient, isothermal compressibility, density and molar volume of the binary system under the present investigation. Theoretical results thus obtained have been compared with experimental findings. Our aim of consideration of single binary system is to describe the temperature and pressure effect on their thermodynamic behaviour.

Thermal expansion coefficient (α) of a binary mixture have been computed using Flory's statistical theory developed for high pressure, vide eq (28), and well justified equation of state developed by Baonza *et al*^{15,16} eq (41) as well as empirical equation based on modified Auerback relation developed Pandey *et al*^{40,41}, vide eq (45) at varying temperature and pressure for the entire mole fraction range, and are reported in Table-1. Thermal expansivity values increase with increase in concentration of the first component of mixture at every temperature and pressure. Trend between experimental and theoretical values of α is observed identical. APD values for each method are also reported in Table-1, a close perusal of which reveals that deviations between theoretical and experimental values increase with increase in temperature and pressure using Flory's statistical theory. The values of α evaluated by eq (41) are in fairly good agreement with experimental values. While maximum deviation between theoretical and experimental findings is observed using eq (45). Thus this relation fails completely at high pressure.

Isothermal compressibility (β_T) values of binary system under the present study are computed using Flory's statistical theory developed for high pressure, eqs (29), (42) and (46) for varying temperature and pressure, The values of β_T are found to be in fair agreement with experimental values for all the three approaches utilized. Careful study of Table-2 shows that eq (42) provides better results than other two methods. Orders of variation of theoretical values of β_T with increases in concentration of first component follow the same trend as experimental values. The values of isothermal compressibility decrease with increase in concentration of first component at all temperatures and pressures. APD values of β_T for the system under consideration using three different methods are reported in Table-2.

Flory's statistical theory developed for high-pressure eqs (38) and (43), vide have been employed for the theoretical prediction of density (ρ) of system under present study. Theoretical and APD values for binary system under investigation at each temperature and pressure are reported in Table-3. The theoretical values of ρ increase with increase in concentration of first component of liquid mixture following the trend shown by experimental density values. At constant temperature, the values of density increase with increase pressure in most of the cases whereas density decreases with increase in temperature at constant pressure. An excellent agreement between theoretical and experimental values of density confirms the validity of present approach. Better assessment of the value is observed using method followed by Baonza *et al*^{15,16} than other two methods.

Abnormal behavior in molar volume is observed at high pressures. Equations (26b) and (44) are employed to compute molar volume of binary mixture under present study. Theoretical and APD values are reported in Table-4. Equation of state, developed by Baonza and coworkers, provides better results than Flory's statistical theory at high pressure developed in the present work. Useful theoretical prediction can be done by observing Table-4 carefully as per requirements.

Adiabatic compressibility and ultrasonic velocity of binary system at different temperatures and pressures are computed with the help of eqs (35) and (40) respectively. Theoretical and APD values of c and β_s are reported in Table-5.

Experimental and theoretical values of ultrasonic velocity increase with increase in concentration of first component of binary liquid mixture. At constant pressure, the values of c decrease with increase in temperature at all the mole fractions, whereas at constant temperature, the values of c decrease with increase in pressure. The values of adiabatic compressibility decrease with increase in concentration of first component of liquid mixture at each temperature and pressure. At constant temperature, β_s decreases with increase in pressure at all the mole fractions under consideration, whereas at constant pressure, its values increase with increase in temperature. An excellent agreement is observed between experimental and theoretical values as evident from Table-5.

Internal pressure of $C_6H_5NO_2 + C_6H_6$ at varying temperatures and pressures have been computed using eq (30) and eq (47), whereas Pseudo Grüneisen parameter is computed using eq (37). Theoretical and APD values of P_i and Γ , thus obtained are reported in Table-6. Internal pressure increases with increase in concentration of the first component of binary system following the trend of its experimental values. At constant temperature, P_i decreases with increase in pressure. Exception is found at only one mole fraction. At constant pressure, its values decrease with increase in temperature at all the mole fractions. Pseudo Grüneisen parameter increases with increase in pressure at constant temperature, whereas reverse trend is observed with increase in temperature at constant pressure.

Heat capacity at constant pressure, heat capacity at constant volume and heat capacities ratio have been evaluated using eq (31), and correlations of eq (36) respectively. Theoretical and APD values for all the three thermodynamic properties are reported in Table-7. The values of C_p and C_v increase with increase in concentration of first component of binary system. At constant temperature, the values of C_p and C_v decrease with increase in pressure at all the mole fraction under consideration, whereas same trend is observed when temperature is varied and pressure is kept constant. The values of heat capacities ratio increase with increase in concentration of the first component at every temperature and pressure. Irregular variations observed on varying temperature at constant pressure or varying pressure at constant temperature.

Table 1. Thermal expansion coefficient (K^{-1}) of $C_6H_5NO_2 + C_6H_6$ at different temperature and varying pressures

T=293.15K

P=0.1MPa

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (Flory)	$\alpha \times 10^3 K$ (Baonza)	$\alpha \times 10^3 K$ (Anjani)	α (Flory%)	α (Baonza%)	α (Anjani%)
0.2	1.026	1.141	1.026	1.110	-11.16	0.00	-8.16
0.4	0.976	0.807	0.976	1.074	17.25	0.00	-10.04
0.6	0.929	0.988	0.929	1.039	-6.38	0.00	-11.89
0.8	0.882	0.932	0.882	1.013	-5.61	0.00	-14.78
APD					10.10	0.00	11.22

P=5.0MPa

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (Flory)	$\alpha \times 10^3 K$ (Baonza)	$\alpha \times 10^3 K$ (Anjani)	α (Flory%)	α (Baonza%)	α (Anjani%)
0.2	1.006	1.102	1.006	1.100	-9.59	-0.02	-9.39
0.4	0.972	1.026	0.972	1.065	-5.53	-0.02	-9.57
0.6	0.917	0.964	0.917	1.032	-5.19	-0.01	-12.63
0.8	0.871	0.913	0.871	1.006	-4.90	-0.01	-15.38
APD					6.30	0.02	11.80

P=10.0MPa

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (Flory)	$\alpha \times 10^3 K$ (Baonza)	$\alpha \times 10^3 K$ (Anjani)	α (Flory%)	α (Baonza%)	α (Anjani%)
0.2	0.991	1.065	0.992	1.091	-7.45	-0.04	-10.05
0.4	0.954	0.996	0.954	1.057	-4.45	-0.03	-10.85
0.6	0.900	0.941	0.900	1.025	-4.57	-0.03	-13.95
0.8	0.855	0.896	0.855	1.000	-4.75	-0.03	-16.99
APD					5.31	0.03	12.96

T=303.15K

P=0.1MPa

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (Flory)	$\alpha \times 10^3 K$ (Baonza)	$\alpha \times 10^3 K$ (Anjani)	α (Flory%)	α (Baonza%)	α (Anjani%)
0.2	1.017	1.130	1.052	1.128	-11.10	-3.41	-10.95
0.4	0.966	1.048	0.995	1.089	-8.51	-2.95	-12.68
0.6	0.920	0.981	0.995	1.063	-6.71	-8.18	-15.59
0.8	0.874	0.926	0.908	1.026	-5.94	-3.89	-17.45
APD					8.06	4.61	14.17

P=5.0MPa

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (Flory)	$\alpha \times 10^3 K$ (Baonza)	$\alpha \times 10^3 K$ (Anjani)	α (Flory%)	α (Baonza%)	α (Anjani%)
0.2	0.997	1.100	1.031	1.118	-10.29	-3.41	-12.13
0.4	0.962	1.027	0.991	1.080	-6.66	-2.98	-12.21
0.6	0.908	0.969	0.982	1.044	-6.74	-8.18	-15.04
0.8	0.863	0.922	0.943	1.018	-6.91	-9.37	-18.01
APD					7.65	5.99	14.35

P=10.0MPa

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (Flory)	$\alpha \times 10^3 K$ (Baonza)	$\alpha \times 10^3 K$ (Anjani)	α (Flory%)	α (Baonza%)	α (Anjani%)
0.2	0.982	1.090	0.983	1.107	-10.98	-0.04	-12.71
0.4	0.944	1.016	0.973	1.071	-7.58	-2.97	-13.43
0.6	0.891	0.957	0.964	1.037	-7.42	-8.19	-16.36
0.8	0.847	0.909	0.880	1.011	-7.34	-3.88	-19.34
				APD	8.33	3.77	15.46

T=313.15K

P=0.1MPa

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (Flory)	$\alpha \times 10^3 K$ (Baonza)	$\alpha \times 10^3 K$ (Anjani)	α (Flory%)	α (Baonza%)	α (Anjani%)
0.2	1.006	1.179	1.071	1.147	-17.21	-6.48	-14.03
0.4	0.957	1.087	1.020	1.107	-13.57	-6.58	-15.64
0.6	0.912	1.015	0.972	1.065	-11.26	-6.59	-16.80
0.8	0.867	0.956	0.987	1.038	-10.32	-13.80	-19.74
				APD	13.09	8.36	16.55

P=5.0MPa

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (Flory)	$\alpha \times 10^3 K$ (Baonza)	$\alpha \times 10^3 K$ (Anjani)	α (Flory%)	α (Baonza%)	α (Anjani%)
0.2	0.986	1.135	1.050	1.134	-15.10	-6.46	-15.02
0.4	0.954	1.053	1.016	1.096	-10.40	-6.59	-14.94
0.6	0.900	0.988	1.532	1.057	-9.78	-0.02	-17.38
0.8	0.856	0.936	1.025	1.030	-9.37	-19.79	-20.34
				APD	11.16	8.22	16.92

P=10.0MPa

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (Flory)	$\alpha \times 10^3 K$ (Baonza)	$\alpha \times 10^3 K$ (Anjani)	α (Flory%)	α (Baonza%)	α (Anjani%)
0.2	0.972	1.093	0.972	1.123	-12.43	-0.04	-15.51
0.4	0.936	1.020	0.997	1.086	-8.94	-6.57	-16.04
0.6	0.884	0.962	0.942	1.048	-8.88	-6.56	-18.60
0.8	0.841	0.916	0.956	1.023	-8.99	-13.77	-21.67
				APD	9.81	6.74	17.96

Table 2. Isothermal compressibility (TPa^{-1}) of $\text{C}_6\text{H}_5\text{NO}_2 + \text{C}_6\text{H}_6$ at different temperature and varying pressures:

T=293.15K

P=0.1MPa

x_1	$\beta_T(\text{TPa}^{-1})$ (Exp)	$\beta_T(\text{TPa}^{-1})$ Flory	$\beta_T(\text{TPa}^{-1})$ Boanza	$\beta_T(\text{TPa}^{-1})$ Anjani	β_T Flory%	β_T Boanza%	β_T Anjani%
0.2	77.70	75.19	77.70	79.48	3.22	-0.01	-2.29
0.4	66.61	65.87	66.62	69.56	1.11	-0.01	-4.42
0.6	60.43	58.71	60.44	61.11	2.86	0.00	-1.11
0.8	53.39	53.04	53.40	55.02	0.66	0.00	-3.04
				APD	1.96	0.00	2.72

P=5.0MPa

x_1	$\beta_T(\text{TPa}^{-1})$ (Exp)	$\beta_T(\text{TPa}^{-1})$ Flory	$\beta_T(\text{TPa}^{-1})$ Boanza	$\beta_T(\text{TPa}^{-1})$ Anjani	β_T Flory%	β_T Boanza%	β_T Anjani%
0.2	78.00	74.88	77.68	76.77	4.00	0.41	1.57
0.4	66.84	65.58	66.60	67.39	1.88	0.36	-0.83
0.6	60.61	58.48	60.42	59.48	3.52	0.32	1.86
0.8	53.54	52.90	53.38	53.71	1.19	0.29	-0.32
				APD	2.65	0.35	1.15

P=10.0MPa

x_1	$\beta_T(\text{TPa}^{-1})$ (Exp)	$\beta_T(\text{TPa}^{-1})$ Flory	$\beta_T(\text{TPa}^{-1})$ Boanza	$\beta_T(\text{TPa}^{-1})$ Anjani	β_T Flory%	β_T Boanza%	β_T Anjani%
0.2	78.30	74.57	77.65	76.30	4.76	0.83	2.55
0.4	67.05	65.31	66.58	65.44	2.60	0.71	2.41
0.6	60.80	58.27	60.41	57.86	4.16	0.64	4.83
0.8	53.68	52.76	53.37	52.40	1.71	0.57	2.38
				APD	3.31	0.69	3.04

T=303.15K

P=0.1MPa

x_1	$\beta_T(\text{TPa}^{-1})$ (Exp)	$\beta_T(\text{TPa}^{-1})$ Flory	$\beta_T(\text{TPa}^{-1})$ Boanza	$\beta_T(\text{TPa}^{-1})$ Anjani	β_T Flory%	β_T Boanza%	β_T Anjani%
0.2	81.56	87.78	81.57	86.08	-7.62	-0.01	-5.54
0.4	70.24	75.43	70.24	74.62	-7.40	-0.01	-6.25
0.6	69.32	66.04	69.32	67.95	4.72	-0.01	1.97
0.8	56.54	58.72	56.54	58.94	-3.85	-0.01	-4.24
				APD	5.90	0.01	4.50

P=5.0MPa

x_1	$\beta_T(\text{TPa}^{-1})$ (Exp)	$\beta_T(\text{TPa}^{-1})$ Flory	$\beta_T(\text{TPa}^{-1})$ Boanza	$\beta_T(\text{TPa}^{-1})$ Anjani	β_T Flory%	β_T Boanza%	β_T Anjani%
0.2	76.73	87.26	81.54	82.98	-13.72	-6.27	-8.14
0.4	81.90	75.32	70.22	72.28	8.03	14.26	11.75
0.6	69.58	66.46	69.30	63.19	4.49	0.40	9.19
0.8	56.70	59.64	56.53	57.04	-5.19	0.30	-0.60
				APD	7.86	5.31	7.42

P=10.0MPa

x_1	$\beta_T(\text{TPa}^{-1})$ (Exp)	$\beta_T(\text{TPa}^{-1})$ Flory	$\beta_T(\text{TPa}^{-1})$ Boanza	$\beta_T(\text{TPa}^{-1})$ Anjani	β_T Flory%	β_T Boanza%	β_T Anjani%
0.2	82.23	86.99	81.51	79.89	-5.79	0.87	2.84
0.4	70.48	75.15	70.20	70.00	-6.62	0.41	0.69
0.6	69.80	66.32	69.28	61.42	4.98	0.74	12.00
0.8	56.86	59.51	56.52	55.50	-4.66	0.60	2.39
				APD	5.51	0.65	4.48

T=313.15K

P=0.1MPa

x_1	$\beta_T(\text{TPa}^{-1})$ (Exp)	$\beta_T(\text{TPa}^{-1})$ Flory	$\beta_T(\text{TPa}^{-1})$ Boanza	$\beta_T(\text{TPa}^{-1})$ Anjani	β_T Flory%	β_T Boanza%	β_T Anjani%
0.2	84.59	102.52	84.59	93.23	-21.20	-0.01	-10.22
0.4	73.87	87.31	73.88	80.88	-18.20	-0.01	-9.48
0.6	66.18	76.13	66.19	69.41	-15.03	-0.01	-4.88
0.8	66.75	67.61	66.75	62.64	-1.29	-0.01	6.16
APD					13.93	0.01	7.68

P=5.0MPa

x_1	$\beta_T(\text{TPa}^{-1})$ (Exp)	$\beta_T(\text{TPa}^{-1})$ Flory	$\beta_T(\text{TPa}^{-1})$ Boanza	$\beta_T(\text{TPa}^{-1})$ Anjani	β_T Flory%	β_T Boanza%	β_T Anjani%
0.2	84.95	101.47	84.56	89.22	-19.45	0.45	-5.03
0.4	74.14	86.52	73.85	77.84	-16.68	0.39	-4.99
0.6	66.40	75.55	66.17	67.19	-13.79	0.35	-1.19
0.8	66.99	67.22	66.73	60.66	-0.33	0.39	9.45
APD					12.56	0.40	5.17

P=10.0MPa

x_1	$\beta_T(\text{TPa}^{-1})$ (Exp)	$\beta_T(\text{TPa}^{-1})$ Flory	$\beta_T(\text{TPa}^{-1})$ Boanza	$\beta_T(\text{TPa}^{-1})$ Anjani	β_T Flory%	β_T Boanza%	β_T Anjani%
0.2	85.30	100.45	84.53	85.64	-17.76	0.90	-0.39
0.4	74.42	85.74	73.83	75.00	-15.21	0.79	-0.78
0.6	66.62	74.99	66.15	65.09	-12.56	0.71	2.29
0.8	67.19	66.83	66.71	58.99	0.53	0.71	12.21
APD					11.52	0.78	3.91

Table 3. density (gm/cm^3) of $\text{C}_6\text{H}_5\text{NO}_2 + \text{C}_6\text{H}_6$ at different temperature and varying pressures

T=293.15K

P=0.1MPa

x_1	$\rho(\text{gm}/\text{cm}^3)$ (Exp)	$\rho(\text{gm}/\text{cm}^3)$ Flory	$\rho(\text{gm}/\text{cm}^3)$ Boanza	ρ Flory%	ρ Boanza%
0.2	0.9546	0.9544	0.9546	0.02	0.00
0.4	1.0242	1.0240	1.0242	0.02	0.00
0.6	1.0965	1.0886	1.0965	0.72	0.00
0.8	1.1478	1.1487	1.1478	-0.07	0.00
APD				0.21	0.00

P=5.0MPa

x_1	$\rho(\text{gm}/\text{cm}^3)$ (Exp)	$\rho(\text{gm}/\text{cm}^3)$ Flory	$\rho(\text{gm}/\text{cm}^3)$ Boanza	ρ Flory%	ρ Boanza%
0.2	0.9583	0.9588	0.9587	-0.05	-0.04
0.4	1.0277	1.0279	1.0280	-0.02	-0.03
0.6	1.0998	1.0919	1.1001	0.72	-0.03
0.8	1.1509	1.1513	1.1512	-0.03	-0.03
APD				0.21	0.03

P=10.0MPa

x_1	$\rho(\text{gm/cm}^3)$ (Exp)	$\rho(\text{gm/cm}^3)$ Flory	$\rho(\text{gm/cm}^3)$ Boanza	ρ Flory%	ρ Boanza%
0.2	0.9620	0.9634	0.9627	-0.14	-0.08
0.4	1.0311	1.0323	1.0318	-0.12	-0.07
0.6	1.1031	1.0960	1.1038	0.65	-0.06
0.8	1.1539	1.1550	1.1545	-0.10	-0.05
			APD	0.25	0.06

T=303.15K

P=0.1MPa

x_1	$\rho(\text{gm/cm}^3)$ (Exp)	$\rho(\text{gm/cm}^3)$ Flory	$\rho(\text{gm/cm}^3)$ Boanza	ρ Flory%	ρ Boanza%
0.2	0.9458	0.9335	0.9549	1.31	-0.96
0.4	1.0139	1.0037	0.9304	1.02	8.23
0.6	1.0857	1.0691	1.0987	1.55	-1.20
0.8	1.1369	1.1302	1.1474	0.59	-0.92
			APD	1.12	2.83

P=5.0MPa

x_1	$\rho(\text{gm/cm}^3)$ (Exp)	$\rho(\text{gm/cm}^3)$ Flory	$\rho(\text{gm/cm}^3)$ Boanza	ρ Flory%	ρ Boanza%
0.2	0.9497	0.9387	0.9589	1.17	-0.97
0.4	1.0175	1.0080	0.9339	0.94	8.22
0.6	1.0891	1.0721	1.1024	1.58	-1.22
0.8	1.1401	1.1317	1.1508	0.74	-0.94
			APD	1.11	2.84

P=10.0MPa

x_1	$\rho(\text{gm/cm}^3)$ (Exp)	$\rho(\text{gm/cm}^3)$ Flory	$\rho(\text{gm/cm}^3)$ Boanza	ρ Flory%	ρ Boanza%
0.2	0.9535	0.9436	0.9630	1.05	-1.00
0.4	1.0211	1.0127	0.9373	0.83	8.21
0.6	1.0925	1.0765	1.1060	1.48	-1.24
0.8	1.1433	1.1357	1.1541	0.67	-0.94
			APD	1.01	2.85

T=313.15K

P=0.1MPa

x_1	$\rho(\text{gm/cm}^3)$ (Exp)	$\rho(\text{gm/cm}^3)$ Flory	$\rho(\text{gm/cm}^3)$ Boanza	ρ Flory%	ρ Boanza%
0.2	0.9354	0.9126	0.9548	2.49	-2.08
0.4	1.0044	0.9821	0.9301	2.27	7.40
0.6	1.0765	1.0465	1.0961	2.87	-1.82
0.8	1.1279	1.1063	1.1504	1.95	-1.99
			APD	2.40	3.32

P=5.0MPa

x_1	$\rho(\text{gm/cm}^3)$ (Exp)	$\rho(\text{gm/cm}^3)$ Flory	$\rho(\text{gm/cm}^3)$ Boanza	ρ Flory%	ρ Boanza%
0.2	0.9394	0.9184	0.9589	2.29	-2.08
0.4	1.0081	0.9875	0.9336	2.09	7.39
0.6	1.0800	1.0514	1.0997	2.72	-1.83
0.8	1.1312	1.1107	1.1538	1.85	-2.00
			APD	2.24	3.32

P=10.0MPa

x_1	$\rho(\text{gm/cm}^3)$ (Exp)	$\rho(\text{gm/cm}^3)$ Flory	$\rho(\text{gm/cm}^3)$ Boanza	ρ Flory%	ρ Boanza%
0.2	0.9433	0.9241	0.9630	2.08	-2.09
0.4	1.0118	0.9928	0.9370	1.92	7.39
0.6	1.0836	1.0562	1.1034	2.59	-1.83
0.8	1.1345	1.1150	1.1571	1.75	-1.99
			APD	2.08	3.32

Table 4. molar volume (cm^3/mol) of $\text{C}_6\text{H}_5\text{NO}_2+\text{C}_6\text{H}_6$ at different temperature and varying pressures: $T=293.15\text{K}$

P=0.1MPa

x_1	V (cm^3/mol) (Exp)	V (cm^3/mol) Flory	V (cm^3/mol) Boanza	V Flory%	V Boanza%
0.2	91.25	91.27	91.25	-0.02	0.00
0.4	93.84	93.85	93.84	-0.02	0.00
0.6	95.86	96.55	95.86	-0.72	0.00
0.8	99.42	99.34	99.42	0.07	0.00
			APD	0.21	0.00

P=5.0MPa

x_1	V (cm^3/mol) (Exp)	V (cm^3/mol) Flory	V (cm^3/mol) Boanza	V Flory%	V Boanza%
0.2	90.90	90.85	90.94	0.05	-0.04
0.4	93.52	93.50	93.55	0.02	-0.03
0.6	95.57	96.26	95.60	-0.72	-0.03
0.8	99.15	99.12	99.17	0.03	-0.03
			APD	0.21	0.03

P=10.0MPa

x_1	V (cm^3/mol) (Exp)	V (cm^3/mol) Flory	V (cm^3/mol) Boanza	V Flory%	V Boanza%
0.2	90.55	90.42	90.62	0.14	-0.08
0.4	93.21	93.10	93.27	0.12	-0.07
0.6	95.29	95.90	95.34	-0.65	-0.06
0.8	98.89	98.79	98.94	0.10	-0.05
			APD	0.25	0.06

T=303.15K

P=0.1MPa

x_1	V (cm^3/mol) (Exp)	V (cm^3/mol) Flory	V (cm^3/mol) Boanza	V Flory%	V Boanza%
0.2	91.25	93.31	91.25	-1.31	0.00
0.4	93.84	95.76	93.84	-1.02	0.00
0.6	95.86	98.32	95.86	-1.55	0.00
0.8	99.42	100.96	99.42	-0.59	0.00
			APD	1.12	0.00

P=5.0MPa

x_1	V (cm ³ /mol ⁻¹) (Exp)	V (cm ³ /mol ⁻¹) Flory	V (cm ³ /mol ⁻¹) Boanza	V Flory%	V Boanza%
0.2	90.90	92.80	90.94	-1.17	-0.04
0.4	93.52	95.35	93.55	-0.94	-0.03
0.6	95.57	98.04	95.60	-1.58	-0.03
0.8	99.15	100.83	99.17	-0.74	-0.03
			APD	1.11	0.03

P=10.0MPa

x_1	V (cm ³ /mol ⁻¹) (Exp)	V (cm ³ /mol ⁻¹) Flory	V (cm ³ /mol ⁻¹) Boanza	V Flory%	V Boanza%
0.2	90.55	92.32	90.62	-1.05	-0.08
0.4	93.21	94.91	93.27	-0.83	-0.07
0.6	95.29	97.64	95.34	-1.48	-0.06
0.8	98.89	100.47	98.94	-0.67	-0.05
			APD	1.01	0.06

T=313.15K

P=0.1MPa

x_1	V (cm ³ /mol ⁻¹) (Exp)	V (cm ³ /mol ⁻¹) Flory	V (cm ³ /mol ⁻¹) Boanza	V Flory%	V Boanza%
0.2	93.13	95.45	119.57	-2.49	-28.39
0.4	95.69	97.86	93.20	-2.27	2.60
0.6	97.64	100.44	87.62	-2.87	10.26
0.8	101.17	103.15	76.06	-1.95	24.82
			APD	2.40	16.52

P=5.0MPa

x_1	V (cm ³ /mol ⁻¹) (Exp)	V (cm ³ /mol ⁻¹) Flory	V (cm ³ /mol ⁻¹) Boanza	V Flory%	V Boanza%
0.2	92.73	94.85	119.15	-2.29	-28.49
0.4	95.34	97.33	92.91	-2.09	2.55
0.6	97.32	99.97	87.38	-2.72	10.21
0.8	100.88	102.74	75.88	-1.85	24.78
			APD	2.24	16.51

P=10.0MPa

x_1	V (cm ³ /mol ⁻¹) (Exp)	V (cm ³ /mol ⁻¹) Flory	V (cm ³ /mol ⁻¹) Boanza	V Flory%	V Boanza%
0.2	92.35	94.27	118.74	-2.08	-28.58
0.4	94.99	96.81	92.64	-1.92	2.48
0.6	97.00	99.52	87.15	-2.60	10.16
0.8	100.58	102.34	75.70	-1.75	24.74
			APD	2.08	16.49

Table 5. adiabatic compressibility (Tpa^{-1}) and ultrasonic velocity (m/s) of $\text{C}_6\text{H}_5\text{NO}_2 + \text{C}_6\text{H}_6$ at different temperature and varying pressures

$T=293.15\text{K}$

$P=0.1\text{MPa}$

x_1	$c(\text{m/s})$ (Exp)	$\beta s(\text{Tpa}^{-1})$ (Exp)	$c(\text{m/s})$ (Theo)	$\beta s(\text{Tpa}^{-1})$ (Theo)	c (%)	βs (%)
0.2	1353.90	57.15	1357.55	56.85	-0.27	0.51
0.4	1380.90	51.20	1309.75	56.93	5.15	-11.18
0.6	1407.80	46.02	1419.13	45.61	-0.81	0.88
0.8	1439.10	42.07	1445.84	41.65	-0.47	1.00
APD				1.67	3.39	

$P=5.0\text{MPa}$

x_1	$c(\text{m/s})$ (Exp)	$\beta s(\text{Tpa}^{-1})$ (Exp)	$c(\text{m/s})$ (Theo)	$\beta s(\text{Tpa}^{-1})$ (Theo)	c (%)	βs (%)
0.2	1374.00	55.27	1382.30	54.58	-0.60	1.25
0.4	1399.70	49.67	1413.09	48.72	-0.96	1.91
0.6	1424.00	44.84	1440.77	44.12	-1.18	1.61
0.8	1453.90	41.10	1465.81	40.43	-0.82	1.65
APD				0.89	2.20	

$P=10\text{MPa}$

x_1	$c(\text{m/s})$ (Exp)	$\beta s(\text{Tpa}^{-1})$ (Exp)	$c(\text{m/s})$ (Theo)	$\beta s(\text{Tpa}^{-1})$ (Theo)	c (%)	βs (%)
0.2	1394.70	53.44	1407.67	52.38	-0.93	1.97
0.4	1417.70	48.25	1436.25	46.96	-1.31	2.68
0.6	1441.00	43.66	1461.89	42.69	-1.45	2.21
0.8	1469.40	40.14	1485.01	39.26	-1.06	2.19
APD				1.19	2.26	

$T=303.15\text{K}$

$P=0.1\text{MPa}$

x_1	$c(\text{m/s})$ (Exp)	$\beta s(\text{Tpa}^{-1})$ (Exp)	$c(\text{m/s})$ (Theo)	$\beta s(\text{Tpa}^{-1})$ (Theo)	c (%)	βs (%)
0.2	1309.00	61.71	1253.66	68.16	4.23	-10.46
0.4	1342.20	54.75	1296.39	59.28	3.41	-8.29
0.6	1344.40	50.96	1335.39	52.45	0.67	-2.93
0.8	1399.30	44.92	1371.18	47.06	2.01	-4.76
APD				2.58	6.61	

$P=5.0\text{MPa}$

x_1	$c(\text{m/s})$ (Exp)	$\beta s(\text{Tpa}^{-1})$ (Exp)	$c(\text{m/s})$ (Theo)	$\beta s(\text{Tpa}^{-1})$ (Theo)	c (%)	βs (%)
0.2	1329.60	59.56	1282.44	64.77	3.55	-8.75
0.4	1360.60	53.09	1319.35	56.99	3.03	-7.35
0.6	1390.70	47.48	1351.65	51.05	2.81	-7.54
0.8	1419.70	43.52	1380.19	46.39	2.78	-6.59
APD				3.04	7.56	

P=10MPa

x_1	$\alpha(\text{m/s})$ (Exp)	$\beta s(\text{Tpa}^{-1})$ (Exp)	$\alpha(\text{m/s})$ (Theo)	$\beta s(\text{Tpa}^{-1})$ (Theo)	c (%)	βs %
0.2	1351.40	57.43	1314.32	61.35	2.74	-6.83
0.4	1379.40	51.47	1345.83	54.52	2.43	-5.92
0.6	1407.60	46.20	1374.26	49.18	2.37	-6.47
0.8	1436.60	42.38	1399.98	44.92	2.55	-6.00
APD					2.52	6.31

T=313.15K

P=0.1MPa

x_1	$\alpha(\text{m/s})$ (Exp)	$\beta s(\text{Tpa}^{-1})$ (Exp)	$\alpha(\text{m/s})$ (Theo)	$\beta s(\text{Tpa}^{-1})$ (Theo)	c (%)	βs %
0.2	1267.10	66.59	1177.10	79.08	7.10	-18.77
0.4	1297.40	59.15	1216.06	68.85	6.27	-16.41
0.6	1337.20	51.95	1250.83	61.08	6.46	-17.56
0.8	1365.30	47.56	1282.10	54.99	6.09	-15.62
APD					6.48	17.09

P=5.0MPa

x_1	$\alpha(\text{m/s})$ (Exp)	$\beta s(\text{Tpa}^{-1})$ (Exp)	$\alpha(\text{m/s})$ (Theo)	$\beta s(\text{Tpa}^{-1})$ (Theo)	c (%)	βs %
0.2	1291.60	63.81	1203.82	75.13	6.80	-17.75
0.4	1319.60	56.97	1239.78	65.88	6.05	-15.65
0.6	1356.20	50.34	1272.08	58.78	6.20	-16.76
0.8	1383.90	46.16	1301.20	53.18	5.98	-15.21
APD					6.26	16.34

P=10MPa

x_1	$\alpha(\text{m/s})$ (Exp)	$\beta s(\text{Tpa}^{-1})$ (Exp)	$\alpha(\text{m/s})$ (Theo)	$\beta s(\text{Tpa}^{-1})$ (Theo)	c (%)	βs %
0.2	1314.70	61.33	1226.44	71.95	6.71	-17.30
0.4	1340.70	54.98	1260.95	63.35	5.95	-15.22
0.6	1374.80	48.83	1291.97	56.72	6.03	-16.17
0.8	1400.70	44.93	1319.87	51.48	5.77	-14.59
APD					6.11	15.82

Table 6. Pseudo Gruneisun parameter and Internal Pressure(dyne/cm²) ultrasonic velocity (m/s) of C₆H₅NO₂+C₆H₆ at different temperature and varying pressures

T=293.15K

P=0.1 MPa

x_1	Γ	P_i	Γ	P_i	P_i	Γ	P_i	P_i
	(Exp)	10 ⁷ dyne/cm ² (Exp)	(Flory)	10 ⁷ dyne/cm ² (Flory)	10 ⁷ dyne/cm ² (Anjani)	Flory%	Flory%	(Anjani)%
0.2	1.1951	387.22	0.9644	444.67	409.43	19.30	-14.83	-5.73
0.4	1.0522	429.39	0.6641	359.20	452.52	36.88	16.35	-5.38
0.6	1.1505	450.61	0.9910	493.34	498.65	13.86	-9.48	-10.66
0.8	1.0410	484.35	1.0020	514.79	539.49	3.74	-6.29	-11.38
APD						18.45	11.74	8.29

P=5.0 MPa

x_1	Γ (Exp)	P_i 10^7 dyne/cm^2 (Exp)	Γ (Flory)	P_i 10^7 dyne/cm^2 (Flory)	P_i 10^7 dyne/cm^2 (Anjani)	Γ Flory%	P_i Flory%	P_i (Anjani)%
0.2	1.3940	378.09	1.1504	426.62	420.20	17.48	-12.84	-11.14
0.4	1.2133	426.36	1.1510	453.58	463.34	5.14	-6.38	-8.67
0.6	1.3092	443.32	1.1515	478.35	508.81	12.04	-7.90	-14.77
0.8	1.1849	476.79	1.1520	501.21	549.31	2.77	-5.12	-15.21
					APD	9.36	8.06	12.45

P=10.0 MPa

x_1	Γ (Exp)	P_i 10^7 dyne/cm^2 (Exp)	Γ (Flory)	P_i 10^7 dyne/cm^2 (Flory)	P_i 10^7 dyne/cm^2 (Anjani)	Γ Flory%	P_i Flory%	P_i (Anjani)%
0.2	1.6009	371.11	1.3566	408.67	419.11	15.26	-10.12	-12.94
0.4	1.3935	416.96	1.3379	437.15	473.60	3.99	-4.84	-13.58
0.6	1.4884	433.85	1.3226	463.38	519.51	11.14	-6.81	-19.74
0.8	1.3458	466.95	1.3098	487.63	559.57	2.67	-4.43	-19.84
					APD	8.27	6.55	16.52

T=303.15K

P=0.1 MPa

x_1	Γ (Exp)	P_i 10^7 dyne/cm^2 (Exp)	Γ (Flory)	P_i 10^7 dyne/cm^2 (Flory)	P_i 10^7 dyne/cm^2 (Anjani)	Γ Flory%	P_i Flory%	P_i (Anjani)%
0.2	1.0440	377.93	0.8408	390.04	397.32	19.47	-3.20	-5.13
0.4	0.5743	457.92	0.8570	421.19	442.23	11.27	-1.01	-6.06
0.6	1.2920	402.25	0.8709	450.40	474.30	32.59	-11.97	-17.91
0.8	0.9765	468.49	0.8829	477.82	527.86	9.59	-1.99	-12.67
					APD	18.23	4.54	10.44

P=5.0 MPa

x_1	Γ (Exp)	P_i 10^7 dyne/cm^2 (Exp)	Γ (Flory)	P_i 10^7 dyne/cm^2 (Flory)	P_i 10^7 dyne/cm^2 (Anjani)	Γ Flory%	P_i Flory%	P_i (Anjani)%
0.2	0.9537	393.87	1.0413	377.00	408.41	-9.18	4.28	-3.69
0.4	1.8599	356.26	1.0336	408.14	452.96	44.43	-14.56	-27.14
0.6	0.9940	673.20	1.0274	436.96	501.01	39.28	-10.49	-26.68
0.8	1.1008	485.33	1.0222	463.73	540.96	11.76	-0.55	-17.30
					APD	26.16	7.47	18.70

P=10.0 MPa

x_1	Γ (Exp)	P_i 10^7 dyne/cm^2 (Exp)	Γ (Flory)	P_i 10^7 dyne/cm^2 (Flory)	P_i 10^7 dyne/cm^2 (Anjani)	Γ Flory%	P_i Flory%	P_i (Anjani)%
0.2	1.4501	362.20	1.2644	369.96	420.17	12.81	-2.14	-16.00
0.4	1.2903	406.22	1.2285	399.89	463.95	4.79	1.56	-14.21
0.6	1.8910	387.04	1.2005	427.56	511.76	36.52	-10.47	-32.22
0.8	1.3303	451.66	1.1779	453.21	552.19	11.46	-0.34	-22.26
					APD	16.39	3.63	21.17

T=313.15K

P=0.1 MPa

x_1	Γ (Exp)	P_i 10^7 dyne/cm^2 (Exp)	Γ (Flory)	P_i 10^7 dyne/cm^2 (Flory)	P_i 10^7 dyne/cm^2 (Anjani)	Γ Flory%	P_i Flory%	P_i (Anjani)%
0.2	0.8585	372.31	0.8028	359.95	385.19	6.48	3.32	-3.46
0.4	0.8306	405.69	0.7878	389.71	428.52	5.16	3.94	-5.63
0.6	0.9593	431.51	0.7758	417.27	480.58	19.13	3.30	-11.37
0.8	1.4857	406.71	0.7661	442.87	518.93	48.43	-8.89	-27.59
					APD	19.80	4.86	12.01

P=5.0 MPa

x_1	Γ (Exp)	P_i 10^7 dyne/cm^2 (Exp)	Γ (Flory)	P_i 10^7 dyne/cm^2 (Flory)	P_i 10^7 dyne/cm^2 (Anjani)	Γ Flory%	P_i Flory%	P_i (Anjani)%
0.2	1.0727	363.52	0.9862	345.29	398.11	8.07	5.02	-9.51
0.4	1.0099	402.75	0.9499	376.05	440.92	5.94	6.63	-16.00
0.6	0.6648	722.63	0.9224	404.57	492.45	18.48	4.70	-32.91
0.8	1.6014	420.76	0.9007	431.10	531.68	46.52	-7.76	-16.97
					APD	19.75	6.03	19.3

P=10.0 MPa

x_1	Γ (Exp)	P_i 10^7 dyne/cm^2 (Exp)	Γ (Flory)	P_i 10^7 dyne/cm^2 (Flory)	P_i 10^7 dyne/cm^2 (Anjani)	Γ Flory%	P_i Flory%	P_i (Anjani)%
0.2	1.2839	356.81	1.1578	330.65	410.53	9.82	7.33	-15.06
0.4	1.2058	393.83	1.1067	362.40	453.47	8.22	7.98	-15.14
0.6	1.3167	415.46	1.0687	391.87	504.30	18.83	5.68	-21.38
0.8	1.8825	391.79	1.0393	419.29	542.97	44.79	-7.02	-38.59
					APD	20.42	7.00	22.54

Table 7. specific heat capacity at constant pressure, specific heat capacity at constant volume and specific heat capacity ratio of $C_6H_5NO_2+C_6H_6$ at different temperature and varying pressures

T=293.15K

P=0.1MPa

x_1	C_p $Jmol^{-1}K^{-1}$ (Exp)	C_v $Jmol^{-1}K^{-1}$ (Exp)	Gamma (Exp)	C_p $Jmol^{-1}K^{-1}$ Flory	C_v $Jmol^{-1}K^{-1}$ Flory	Gamma Flory	C_p %	C_v %	Gamma %
0.2	137.13	100.86	1.3596	189.90	143.59	1.323	-38.49	-29.76	2.72
0.4	169.95	130.64	1.3010	200.44	173.21	1.157	-17.94	-24.58	11.05
0.6	168.20	128.07	1.3133	211.08	164.00	1.287	-25.49	-21.91	2.00
0.8	200.27	157.79	1.2692	221.78	174.13	1.274	-10.74	-9.38	-0.35
						APD	-23.17	-21.41	4.03

P=5.0MPa

x_1	C_p $Jmol^{-1}K^{-1}$ (Exp)	C_v $Jmol^{-1}K^{-1}$ (Exp)	Gamma (Exp)	C_p $Jmol^{-1}K^{-1}$ Flory	C_v $Jmol^{-1}K^{-1}$ Flory	Gamma Flory	C_p %	C_v %	Gamma %
0.2	118.67	84.10	1.4111	159.51	116.28	1.372	-34.41	-27.67	2.79
0.4	150.86	112.10	1.3458	171.06	127.07	1.346	-13.39	-11.78	-0.03
0.6	149.24	110.40	1.3518	182.69	137.83	1.325	-22.42	-19.90	1.95
0.8	196.45	150.83	1.3025	194.40	148.57	1.308	-9.67	-8.39	-0.46
APD							19.97	16.94	1.31

P=10.0 MPa

x_1	C_p $Jmol^{-1}K^{-1}$ (Exp)	C_v $Jmol^{-1}K^{-1}$ (Exp)	Gamma (Exp)	C_p $Jmol^{-1}K^{-1}$ Flory	C_v $Jmol^{-1}K^{-1}$ Flory	Gamma Flory	C_p %	C_v %	Gamma %
0.2	104.91	71.60	1.4652	135.51	95.19	1.424	-29.17	-24.78	2.84
0.4	132.21	95.14	1.3896	147.62	106.15	1.391	-11.66	-10.37	-0.08
0.6	131.94	94.75	1.3926	159.81	117.09	1.365	-21.12	-19.08	1.99
0.8	156.53	117.05	1.3373	172.06	128.03	1.344	-9.93	-8.58	-0.49
APD							17.97	15.70	1.35

T=303.15K

P=0.1MPa

x_1	C_p $Jmol^{-1}K^{-1}$ (Exp)	C_v $Jmol^{-1}K^{-1}$ (Exp)	Gamma (Exp)	C_p $Jmol^{-1}K^{-1}$ Flory	C_v $Jmol^{-1}K^{-1}$ Flory	Gamma Flory	C_p %	C_v %	Gamma %
0.2	140.58	106.35	1.3218	183.95	142.83	1.288	-30.85	-25.54	2.56
0.4	281.67	241.12	1.1682	197.57	155.28	1.272	-17.98	-15.94	0.82
0.6	130.79	96.15	1.3602	211.24	167.77	1.259	-61.51	-42.69	7.43
0.8	193.34	153.61	1.2587	224.95	180.28	1.248	-16.35	-14.80	0.87
APD							31.67	24.74	2.92

P=5.0MPa

x_1	C_p $Jmol^{-1}K^{-1}$ (Exp)	C_v $Jmol^{-1}K^{-1}$ (Exp)	Gamma (Exp)	C_p $Jmol^{-1}K^{-1}$ Flory	C_v $Jmol^{-1}K^{-1}$ Flory	Gamma Flory	C_p %	C_v %	Gamma %
0.2	155.66	120.83	1.2882	151.28	112.30	1.347	2.81	7.59	-4.57
0.4	89.03	57.71	1.5427	166.15	125.71	1.322	-86.61	-54.09	14.33
0.6	305.57	208.50	1.4656	181.09	139.11	1.302	-71.71	-48.27	11.18
0.8	183.40	140.76	1.3029	196.10	152.52	1.286	-18.42	-16.67	1.32
APD							43.48	31.65	7.85

P=10.0 MPa

x_1	C_p $Jmol^{-1}K^{-1}$ (Exp)	C_v $Jmol^{-1}K^{-1}$ (Exp)	Gamma (Exp)	C_p $Jmol^{-1}K^{-1}$ Flory	C_v $Jmol^{-1}K^{-1}$ Flory	Gamma Flory	C_p %	C_v %	Gamma %
0.2	104.23	72.79	1.4319	129.76	91.51	1.4179	-24.50	-20.46	0.97
0.4	129.45	94.52	1.3694	143.98	104.45	1.3780	-11.23	-9.51	-0.66
0.6	94.90	62.82	1.5108	158.29	117.39	1.3480	-66.78	-46.49	10.75
0.8	145.02	108.09	1.3416	172.65	130.33	1.3250	-19.05	-17.06	1.26
APD							30.39	23.38	3.41

T=313.15K

P=0.1MPa

x_1	C_p $Jmol^{-1}K^{-1}$	C_v $Jmol^{-1}K^{-1}$	Gamma	C_p $Jmol^{-1}K^{-1}$	C_v $Jmol^{-1}K^{-1}$	Gamma	C_p	C_v	Gamma
	(Exp)	(Exp)	(Exp)	Flory	Flory	Flory	%	%	%
0.2	153.38	120.74	1.2703	177.20	136.70	1.296	-15.54	-11.68	-2.05
0.4	174.50	139.72	1.2489	196.10	154.64	1.268	-12.38	-9.65	-1.54
0.6	167.26	131.29	1.2740	215.09	172.55	1.247	-28.59	-23.91	2.16
0.8	116.18	82.79	1.4033	234.15	190.45	1.229	-101.5	-56.53	12.39
						APD	39.51	25.44	4.53

P=5.0MPa

x_1	C_p $Jmol^{-1}K^{-1}$	C_v $Jmol^{-1}K^{-1}$	Gamma	C_p $Jmol^{-1}K^{-1}$	C_v $Jmol^{-1}K^{-1}$	Gamma	C_p	C_v	Gamma
	(Exp)	(Exp)	(Exp)	Flory	Flory	Flory	%	%	%
0.2	125.06	93.94	1.3313	145.30	107.58	1.351	-16.18	-12.68	-1.45
0.4	147.94	113.66	1.3016	163.72	124.67	1.313	-10.67	-8.83	-0.89
0.6	143.97	109.15	1.3190	182.22	141.76	1.285	-26.57	-23.00	2.54
0.8	103.96	71.62	1.4514	200.79	158.85	1.264	-93.15	-54.91	12.91
						APD	36.64	24.86	4.45

P=10.0 MPa

x_1	C_p $Jmol^{-1}K^{-1}$	C_v $Jmol^{-1}K^{-1}$	Gamma	C_p $Jmol^{-1}K^{-1}$	C_v $Jmol^{-1}K^{-1}$	Gamma	C_p	C_v	Gamma
	(Exp)	(Exp)	(Exp)	Flory	Flory	Flory	%	%	%
0.2	106.70	76.72	1.3908	123.66	88.57	1.396	-15.90	-13.38	-0.39
0.4	125.52	92.74	1.3534	140.78	104.02	1.353	-12.16	-10.85	0.00
0.6	124.84	91.49	1.3645	157.98	119.49	1.322	-26.55	-23.43	3.11
0.8	93.59	62.58	1.4956	175.24	134.99	1.298	-87.25	-53.64	13.20
						APD	35.46	25.32	3.98

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CHAPTER-V

**THERMODYNAMIC BEHAVIOR OF
TERNARY LIQUID MIXTURES:
APPLICATION OF FLORY
STATISTICAL THEORY WITH
MODIFIED EXPRESSION OF
CHARACTERISTIC PRESSURE**

INTRODUCTION

In recent past Flory's statistical theory of binary liquid mixtures¹⁻⁴ has been applied successfully to multicomponent liquid mixtures for evaluating activity,⁵ surface tension,⁶⁻⁸ excess volume,^{9,10} viscosity,¹¹⁻¹³ sound velocity^{14,16} and related properties.¹⁷⁻¹⁸ Assuming two body interactions only, the Flory theory has been formulated for deducing various properties of multicomponent systems. In addition, two body interaction coefficients between same two molecules are assumed to be equal i.e. $X_{ij}=X_{ji}$. For example, in case of a ternary mixture consisting of molecules i , j and k , it was assumed that $X_{ij}=X_{ji}$, $X_{jk}=X_{kj}$, and $X_{ik}=X_{ki}$. In the present work, it has been demonstrated that Flory theory shows better performance for various thermodynamic properties of ternary systems. If we consider all the interaction parameters, and $X_{ij}\neq X_{ji}$, $X_{jk}\neq X_{kj}$, and $X_{ik}\neq X_{ki}$. Expressions considering all the six interaction parameters are deduced, and the values of molar volume, density, velocity, heat capacity at constant pressure, heat capacity at constant volume, internal pressure, adiabatic compressibility, isothermal compressibility, thermal expansion coefficient, heat capacities ratio and Pseudo Grüneisen parameter of ternary systems namely, toluene(x_1) + n-heptane(x_2) + n-hexane(x_3)-(I), cyclohexane(x_1) + heptane(x_2) + n-hexane(x_3)-(II) and n-hexane(x_1) + heptane(x_2) + n-decane(x_3)-(III).

THEORETICAL

Flory *et al*¹⁴⁻¹⁶ introduced a parameter C to consider the van der Waals energy-volume relationship in cell partition function of Hirschfelder and Eyring. The reduced equation of state derived from resulting partition function is given by¹

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3} - 1} - \frac{1}{\tilde{V}\tilde{T}} \quad (1)$$

where \tilde{P} , \tilde{V} and \tilde{T} are the reduced parameters of pressure, volume and temperature of their respective pure components. Their numerical values can be obtained by using the following relations:

$$\tilde{P} = \frac{P}{P^*} = \frac{2PV^*}{S\eta} = \frac{P\beta_T}{\alpha T\tilde{V}} = \frac{P}{\gamma_P T\tilde{V}} \quad (2)$$

$$\tilde{T} = \frac{T}{T^*} = \frac{2V^*cRT}{S\eta} = \frac{\tilde{V}^{1/3} - 1}{\tilde{V}^{1/3}} \quad (3)$$

$$\tilde{V} = \frac{V}{V^*} = \left[\left(\frac{\alpha T}{3(1 + \alpha T)} \right) + 1 \right]^3 \quad (4)$$

The values of reduced and characteristic parameters obtained in this way are utilized in the resulting expression of excess volume of multi component systems. Considering all the possibilities of two body interactions and the statistical mechanical concept of Flory, intermolecular energy may be written as,

$$E_o = S_1r_1\eta_{11} + S_2r_2\eta_{22} + S_3r_3\eta_{33} - \frac{(\Delta\eta_1A_{12} + \Delta\eta_2A_{23} + \Delta\eta_3A_{31})}{2V} \quad (5)$$

where

$$\Delta\eta_1 = \eta_{11} + \eta_{22} - 2\eta_{12} \quad (6a)$$

$$\Delta\eta_2 = \eta_{22} + \eta_{33} - 2\eta_{23} \quad (6b)$$

$$\Delta\eta_3 = \eta_{33} + \eta_{11} - 2\eta_{31} \quad (6c)$$

It will be assumed that random mixing of three components is taking place. Furthermore, site fraction for ternary systems can be defined as follows:

$$\theta_i = \frac{\psi_i}{\psi_i + \sum_{k \neq i} \psi_k \left(\frac{V_i^*}{V_k^*} \right)^{1/3}} \quad (7)$$

$$\theta_3 = 1 - \theta_1 - \theta_2 = \frac{S_3r_3N_3}{S\bar{F}N} \quad (7a)$$

$$\theta_2 = 1 - \theta_1 - \theta_3 = \frac{S_2r_2N_2}{S\bar{F}N} \quad (7b)$$

On this basis

$$A_{12} = S_1r_1N_1\theta_2 = S_2r_2N_2\theta_3 \quad (8a)$$

$$A_{23} = S_2r_2N_2\theta_3 = S_3r_3N_3\theta_2 \quad (8b)$$

$$A_{31} = S_3r_3N_3\theta_1 = S_1r_1N_1\theta_3 \quad (8c)$$

where

$$\bar{r} = \frac{r_1 N_1 + r_2 N_2 + r_3 N_3}{N}$$

$$S = S_1 r_1 N_1 + S_2 r_2 N_2 + S_3 r_3 N_3$$

$$N = N_1 + N_2 + N_3$$

On substituting eqs (9) and (10) into eq (7), we get

$$-\frac{E_0}{\bar{r}N} = \frac{S}{2V} [\theta_1 \eta_{11} + \theta_2 \eta_{22} + \theta_3 \eta_{33} - \theta_1 \theta_2 \Delta \eta_1 - \theta_2 \theta_3 \Delta \eta_2 - \theta_3 \theta_1 \Delta \eta_3] \quad (9)$$

Defining the segment fractions,

$$\psi_3 = 1 - \psi_1 - \psi_2 = \frac{r_3 N_3}{\bar{r}N} \quad (10a)$$

$$\psi_2 = 1 - \psi_1 - \psi_3 = \frac{r_2 N_2}{\bar{r}N} \quad (10b)$$

we have

$$\frac{1}{\bar{r}} = \frac{\psi_1}{r_1} + \frac{\psi_2}{r_2} + \frac{\psi_3}{r_3} \quad (11)$$

$$S = \psi_1 S_1 + \psi_2 S_2 + \psi_3 S_3 \quad (12)$$

$$\theta_i = \sum \frac{\psi_i S_i}{S} \quad (13)$$

For the present systems, expressions for segment fraction and site fractions are given by ⁶

$$\psi_i = \frac{x_i V_i^*}{\sum x_i V_i^*} \quad (14)$$

and

$$\theta_i = \frac{\psi_i}{\psi_i + \sum_{k \neq i} \psi_k \left(\frac{V_i^*}{V_k^*} \right)^{1/3}} \quad (15)$$

The characteristic pressure of the pure component is given by

$$P_1^* = \frac{S_1 \eta_{11}}{2V^{*2}}, P_2^* = \frac{S_2 \eta_{22}}{2V^{*2}}, P_3^* = \frac{S_3 \eta_{33}}{2V^{*2}} \quad (16)$$

By analogy, we define

$$X_{12} = \frac{S_1 \Delta \eta_1}{2V^{*2}}, X_{23} = \frac{S_2 \Delta \eta_2}{2V^{*2}}, X_{31} = \frac{S_3 \Delta \eta_3}{2V^{*2}} \quad (17)$$

$$X_{21} = \frac{S_2 \Delta \eta_2}{2V^{*2}}, X_{32} = \frac{S_3 \Delta \eta_3}{2V^{*2}}, X_{13} = \frac{S_1 \Delta \eta_1}{2V^{*2}} \quad (18)$$

Using these expressions, we can find

$$\Delta \eta_1 = \frac{(X_{12} + X_{13})V^{*2}}{S_1}, \Delta \eta_2 = \frac{(X_{23} + X_{21})V^{*2}}{S_2}, \Delta \eta_3 = \frac{(X_{31} + X_{32})V^{*2}}{S_3}, \quad (19)$$

From eqs (16), (17) and (11), we get

$$-\frac{E_0}{\bar{F}N} = \frac{S}{2V} \left[\theta_1 \frac{2P_1^* V^{*2}}{S_1} + \theta_2 \frac{2P_2^* V^{*2}}{S_2} + \theta_3 \frac{2P_3^* V^{*2}}{S_3} - \frac{\theta_1 \theta_2 (X_{12} + X_{13})V^{*2}}{S_1} - \frac{\theta_2 \theta_3 (X_{23} + X_{21})V^{*2}}{S_2} - \frac{\theta_1 \theta_3 (X_{13} + X_{12})V^{*2}}{S_1} \right] \quad (20)$$

On simplification, one gets

$$-\frac{E_0}{\bar{F}N} = \frac{V^{*2}}{V} \left[\psi_1 P_1^* + \psi_2 P_2^* + \psi_3 P_3^* - \psi_1 \theta_2 \left(\frac{X_{12} + X_{13}}{2} \right) - \psi_1 \theta_3 \left(\frac{X_{12} + X_{13}}{2} \right) - \psi_2 \theta_3 \left(\frac{X_{23} + X_{21}}{2} \right) \right] \quad (21)$$

By analogy with the energy for a pure component, we define

$$-\frac{E_0}{\bar{F}N} = \frac{P^* V^*}{\bar{V}} = \frac{CKT^*}{\bar{V}} \quad (22)$$

Comparing eqs (18) and (19)

$$P^* = \psi_1 P_1^* + \psi_2 P_2^* + \psi_3 P_3^* - \psi_1 \theta_2 \left(\frac{X_{12} + X_{13}}{2} \right) - \psi_2 \theta_3 \left(\frac{X_{23} + X_{21}}{2} \right) - \psi_3 \theta_1 \left(\frac{X_{31} + X_{32}}{2} \right) \quad (23)$$

which is the modified expression for the characteristic pressure of a ternary liquid mixture as developed in the present work. In the case of multicomponent system, interaction parameter is defined as,²¹

$$X_{ij} = P_i^* \left[1 - \left(\frac{P_i^*}{P_i^*} \right)^{1/2} \left(\frac{V_i^*}{V_i^*} \right)^{1/6} \right]^2 \quad (24)$$

and the characteristic temperature and reduced temperatures are given by^{6,9}

$$T^* = \frac{P^*}{\sum_{i=1}^3 \frac{\psi_i P_i^*}{T_i^*}} \quad (25)$$

and

$$\tilde{T} = \frac{T}{T^*} \quad (26)$$

Ideal reduced volume and the ideal reduced temperature for a multicomponent system are expressed as,

$$\tilde{V}^0 = \sum_{i=1}^3 X_i \tilde{V}_i \quad (27)$$

$$\tilde{T}^0 = \frac{\tilde{V}^0^{1/3} - 1}{\tilde{V}^0^{4/3}} \quad (28)$$

The excess reduced volume is given by ^{2,9}

$$\tilde{V}^E = \tilde{V}^0^{1/3} \left(\frac{4}{3} - \tilde{V}^0^{1/3} \right)^{-1} (\tilde{T} - \tilde{T}^0) \quad (29)$$

The reduced volume for the mixtures can be written as,

$$\tilde{V} = \tilde{V}^E + \tilde{V}^0 \quad (30)$$

$$V^* = \frac{V}{\tilde{V}} \quad (31)$$

Thermal expansion coefficient of the mixture is calculated by the equation

$$\alpha = \frac{3 \left(\tilde{V}^{1/3} - 1 \right)}{T \left(1 - 3 \left(\tilde{V}^{1/3} - 1 \right) \right)} \quad (32)$$

Isothermal compressibility for liquid mixtures can be computed by following expression:

$$\beta_T = \frac{\alpha T \tilde{V}^2}{P^*} \quad (33)$$

Internal pressure (P_i) can be expressed as a function of thermal expansion coefficient (α) and isothermal compressibility (β_T) through the relation

$$P_i = \frac{\alpha T}{\beta_T} \quad (34)$$

$$P_i = \frac{P^*}{\tilde{V}^2} \quad (35)$$

To compute heat capacity at constant pressure and excess heat capacity following expressions have been used. Heat capacity at constant pressure of mixtures (C_p) is defined as,

$$C_p = C_p^E + C_{p(idl)} \quad (36)$$

where $C_{p(idl)}$ is ideal heat capacity of mixture given by

$$C_{p(idl)} = \sum x_i C_{pi} \quad (37)$$

C_{pi} = Heat capacity of i^{th} pure component C_p^E is defined by Khanwalkar *et al*²² according to Flory theory as,

$$C_p^E = \frac{P^* V^*}{T^*} \left[\frac{1}{\left(\frac{4}{3} \tilde{V}^{\frac{1}{3}} - 1 \right)} - \sum_i \left\{ \frac{x_i}{\left(\left(\frac{4}{3} \tilde{V}_i^{\frac{1}{3}} - 1 \right) \right)} \right\} \right] \quad (38)$$

Adiabatic compressibility has been evaluated utilizing well-known thermodynamic relation

$$\beta_T - \beta_s = \frac{\alpha^2 TV}{C_p} \quad (39)$$

which in turn becomes

$$\beta_s = \beta_T - \frac{\alpha^2 TV}{C_p} \quad (40)$$

$$\beta_s = \frac{\alpha T \tilde{V}^2}{P^*} - \frac{\alpha^2 TV}{C_p} \quad (41)$$

$$\beta_s = \frac{\alpha T \tilde{V}}{P^*} \left[\tilde{V} - \frac{\tilde{\alpha}}{\tilde{C}_p} \right] \quad (42)$$

$$\tilde{\alpha} = \alpha T^* \quad (43)$$

$$\tilde{C}_p = \frac{C_p}{\left(\frac{P^* V^*}{T^*} \right)} \quad (44)$$

With the help of eqs (32), β_s , for the mixtures can be calculated.

For the evaluation of density of mixture, following simplifying expression has been taken in to account:

$$\rho = \frac{M}{V} \quad (45)$$

Or

$$\rho = \frac{\sum x_i M_i}{\left(\sum x_i V_i^* \right) \bar{V}} \quad (46)$$

Ultrasonic velocity of mixture has been obtained with the help of following thermodynamic expression

$$c = \left(\frac{1}{\beta_s \rho} \right)^{\frac{1}{2}} \quad (47)$$

$$\frac{\beta_T}{\beta_s} = \frac{C_p}{C_v} = \gamma \quad (48)$$

$$\Gamma = \frac{\gamma - 1}{\alpha T} \quad (49)$$

RESULTS AND DISCUSSION

Molar volume, density, velocity, heat capacity at constant pressure, heat capacity at constant volume, internal pressure, adiabatic compressibility, isothermal compressibility, thermal expansion coefficient, heat capacities ratio and Pseudo-Grüneisen parameter of three ternary liquid mixtures namely toluene + n-heptane + n-hexane (I), Cyclohexane + heptane + n-hexane (II) and n-hexane + heptane + n-decane(III) at 298.15K have been computed at different mole fractions using modified Flory,s statistical theory. Experimental values of pure and multicomponent systems under study have been taken from literature ⁷⁻¹³.

Excess molar volume, density and ultrasonic velocity of ternary systems have been computed using eqs (31), (46) and (47) respectively. Theoretical values, thus obtained, are compared with the experimental findings and are reported in Table-1. A close perusal of Table-1 shows that maximum APD values of density and velocity are found in system I and system III respectively whereas minimum APD values are found in the case of system II for both density and velocity. For system I, there is large percentage deviation between experimental and theoretical values of density of the systems under investigation. But there is close agreement between experimental and

theoretical values for ultrasonic velocity. It can be seen from Table-1 that the computed values of density and velocity decrease with increasing mole fraction x_1 of first component for ternary systems (III) while reverse behavior is observed for rest of the systems. Trends of APD values for ρ and u have following sequence:

For density (ρ),	System I> System III> System II
For velocity (u),	System III> System I> System II

Excess heat capacity at constant pressure (C_p^E), heat capacity at constant pressure (C_p) and that at constant volume (C_v) are evaluated using eqs (38), (36) and (48) respectively. A comparison between theoretical and experimental values has been made in Table-2. In all the ternary liquid mixtures the trend between experimental and computed values of C_p and C_v is the same. The values of C_p and C_v are decreasing with increasing mole fraction x_1 . For ternary liquid system (I), percentage deviation between experimental and computed values is very high. But in case of system (II) and system (III), it is found satisfactorily. Maximum APD is obtained for system II. Order of trend has the following sequence:

For C_p ,	System I> System III> System II
For C_v ,	System I> System III> System II

Internal pressure and adiabatic compressibility values are computed using eqs (35) and (42) respectively. A close perusal of Table-3 shows a close agreement between theoretical and experimental findings. Maximum percentage deviations in values of P_i and β_s are found in system (I) than other systems. Minimum and least APD is obtained in system III and system I respectively. Minimum APD in values of β_s is obtained for system II and maximum APD is seen in system I. Moreover, APD of P_i and β_s for all the three ternary systems have the following trend:

For β_s	System I> System III> System II
For P_i	System I> System III> System II

Thermal expansion coefficient and isothermal compressibility have been computed using the values of reduced pressure, reduced volume and reduced temperature with the help of eqs (32) and (33) respectively. Theoretical and experimental values of α and β_T are reported in Table-4. It is clear from this Table that the values of these thermodynamic properties decrease with increasing concentration

Table 1. Computed and Experimental values of density and ultrasonic velocity with percentage deviation and excess volume of ternary liquid mixtures at 298.15K

x_1	x_2	V^B (Theo) $\text{cm}^3 \text{mol}^{-1}$	ρ (Theo) gm cm^{-3}	c (Theo) m s^{-1}	ρ (Exp) gm cm^{-3}	c (Exp) m s^{-1}	ρ %	C %
0.1210	0.1838	-0.1361	0.6813	1113.75	0.7506	1106.20	9.23	-0.68
0.1459	0.2011	-0.1501	0.6861	1119.94	0.7529	1121.10	8.87	0.10
0.1698	0.2170	-0.1606	0.6908	1125.81	0.7570	1116.90	8.75	-0.80
0.1929	0.2358	-0.1666	0.6953	1131.71	0.7635	1122.00	8.93	-0.86
0.2160	0.2544	-0.1700	0.6999	1137.57	0.7682	1128.30	8.90	-0.82
0.2390	0.2626	-0.1758	0.7042	1142.73	0.7730	1133.80	8.90	-0.79
0.2641	0.2875	-0.1723	0.7093	1149.40	0.7791	1139.90	8.96	-0.83
0.2849	0.3060	-0.1686	0.7134	1154.78	0.7835	1145.30	8.95	-0.83
0.3088	0.3222	-0.1649	0.7181	1160.64	0.7845	1151.50	8.46	-0.79
0.3330	0.3391	-0.1593	0.7229	1166.63	0.7938	1158.00	8.93	-0.75
0.3559	0.3553	-0.1524	0.7274	1172.32	0.8000	1164.40	9.07	-0.68
0.3760	0.3735	-0.1444	0.7315	1177.57	0.8036	1171.30	8.97	-0.53
0.3983	0.3908	-0.1339	0.7359	1183.23	0.8089	1177.20	9.02	-0.51
0.4204	0.3974	-0.1287	0.7402	1188.21	0.8188	1188.00	9.60	-0.02
0.4433	0.4045	-0.1224	0.7447	1193.42	0.8324	1189.60	10.54	-0.32
						APD	9.07	-0.61

[illegible]

Table 3. Computed and experimental values of internal pressure and adiabatic compressibility along with percentage deviation at 298.15K

x_1	x_2	Pi (Theo) 10^7 dyne cm $^{-2}$	$\beta_s(\text{Tpa}^{-1})$ (Theo)	Pi (Exp) 10^7 dyne cm $^{-2}$	$\beta_s(\text{Tpa}^{-1})$ (Exp)	Pi %	β_s %
0.1210	0.1838	256.99	118.33	252.44	108.87	-1.80	-8.69
0.1459	0.2011	259.54	116.20	254.25	105.68	-2.08	-9.96
0.1698	0.2170	261.98	114.02	256.03	105.90	-2.32	-7.76
0.1929	0.2358	264.41	112.03	257.89	104.04	-2.53	-7.68
0.2160	0.2544	266.85	110.42	259.80	102.25	-2.71	-7.99
0.2390	0.2626	269.09	108.75	261.76	100.60	-2.80	-8.10
0.2641	0.2875	271.86	106.72	263.85	98.78	-3.03	-8.04
0.2849	0.3060	274.11	105.11	265.80	97.30	-3.13	-8.03
0.3088	0.3222	276.62	103.37	267.99	96.09	-3.22	-7.58
0.3330	0.3391	279.02	101.64	270.29	93.94	-3.23	-8.20
0.3559	0.3553	281.63	100.03	272.56	92.19	-3.33	-8.50
0.3760	0.3735	283.86	98.59	274.73	90.70	-3.32	-8.70
0.3983	0.3908	286.29	97.06	277.14	89.21	-3.30	-8.79
0.4204	0.3974	288.53	95.69	279.30	86.53	-3.30	-10.58
0.4433	0.4045	290.87	94.28	281.62	84.89	-3.29	-11.07
					APD	-2.89	-8.64

x ₁	x ₂	Pi (Theo) 10 ⁷ dyne cm ⁻²	βs(Tpa ⁻¹) (Theo)	Pi (Exp) 10 ⁷ dyne cm ⁻²	βs(Tpa ⁻¹) (Exp)	Pi %	β _s %
0.1189	0.1823	254.33	121.15	251.58	120.57	-1.09	-0.48
0.1440	0.2012	256.38	119.49	253.24	118.36	-1.24	-0.95
0.1650	0.2203	258.19	118.03	254.74	117.40	-1.35	-0.54
0.1879	0.2379	260.10	116.53	256.34	116.14	-1.47	-0.34
0.2062	0.2484	261.56	115.42	256.56	115.03	-1.55	-0.34
0.2346	0.2729	264.01	113.56	259.71	112.99	-1.65	-0.51
0.2564	0.2903	265.86	112.19	261.37	112.07	-1.72	-0.11
0.2799	0.3073	267.84	110.76	263.16	110.31	-1.78	-0.41
0.3031	0.3266	269.85	109.33	265.05	108.79	-1.81	-0.50
0.3249	0.3424	271.70	108.04	266.08	107.52	-2.11	-0.48
0.3487	0.3599	273.74	106.65	268.78	105.96	-1.85	-0.65
0.3700	0.3776	275.61	105.39	270.66	104.65	-1.83	-0.70
0.3933	0.3948	277.63	104.06	272.70	103.02	-1.81	-1.01
0.4143	0.4030	279.32	102.99	274.40	102.13	-1.79	-0.84
0.4346	0.4103	280.95	101.97	276.19	101.04	-1.72	-0.92
					APD	-1.65	-0.58

Table 5. Computed and experimental values of specific heat capacity ratio (γ) and Pseudo Gruisen parameter (Γ) along with percentage deviation at 298.15K.

x_1	x_2	γ (Theo)	Γ (Theo)	γ (Exp)	Γ (Exp)	γ %	Γ %
0.1210	0.1838	1.2950	0.7490	1.4446	1.1198	10.36	33.11
0.1459	0.2011	1.2956	0.7566	1.4676	1.1859	11.72	36.20
0.1698	0.2170	1.2963	0.7638	1.4449	1.1356	10.29	32.74
0.1929	0.2358	1.2969	0.7710	1.4501	1.1569	10.56	33.36
0.2160	0.2544	1.2975	0.7782	1.4546	1.1765	10.80	33.85
0.2390	0.2626	1.2983	0.7852	1.4575	1.1920	10.92	34.13
0.2641	0.2875	1.2989	0.7933	1.4621	1.2127	11.16	34.59
0.2849	0.3060	1.2995	0.7999	1.4638	1.2252	11.22	34.71
0.3088	0.3222	1.3000	0.8075	1.4599	1.2234	10.95	33.99
0.3330	0.3391	1.3010	0.8153	1.4696	1.2585	11.47	35.22
0.3559	0.3553	1.3017	0.8227	1.4747	1.2809	11.73	35.77
0.3760	0.3735	1.3022	0.8293	1.4772	1.2963	11.85	36.03
0.3983	0.3908	1.3029	0.8366	1.4782	1.3086	11.86	36.07
0.4204	0.3974	1.3037	0.8437	1.5030	1.3847	13.26	39.07
0.4433	0.4045	1.3045	0.8512	1.5097	1.4122	13.59	39.73
APD						11.45	35.24

x ₁	x ₂	γ (Theo)	Γ (Theo)	γ (Exp)	Γ (Exp)	γ %	Γ %
0.1189	0.1823	1.2978	0.7447	1.3228	0.8045	1.89	7.43
0.1440	0.2012	1.2987	0.7508	1.3322	0.8319	2.51	9.74
0.1650	0.2203	1.2997	0.7566	1.3293	0.8284	2.23	8.67
0.1879	0.2379	1.3007	0.7628	1.3294	0.8322	2.16	8.34
0.2062	0.2484	1.3017	0.7677	1.3315	0.8404	2.24	8.66
0.2346	0.2729	1.3030	0.7755	1.3363	0.8575	2.50	9.56
0.2564	0.2903	1.3040	0.7816	1.3327	0.8522	2.16	8.29
0.2799	0.3073	1.3051	0.7881	1.3385	0.8712	2.49	9.54
0.3031	0.3266	1.3062	0.7946	1.3410	0.8819	2.59	9.90
0.3249	0.3424	1.3073	0.8001	1.3419	0.8882	2.58	9.92
0.3487	0.3599	1.3084	0.8074	1.3451	0.9008	2.73	10.36
0.3700	0.3776	1.3094	0.8135	1.3462	0.9079	2.73	10.39
0.3933	0.3948	1.3105	0.8202	1.3505	0.9238	2.96	11.21
0.4143	0.4030	1.3117	0.8261	1.3490	0.9232	2.76	10.51
0.4346	0.4103	1.3129	0.8319	1.3496	0.9283	2.72	10.39
APD						2.48	9.53

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CHAPTER-VI

THERMODYNAMIC PROPERTIES OF METAL ALLOYS: APPLICATION OF FLORY'S STATISTICAL THEORY

INTRODUCTION

The study of physico-chemical behavior of metal alloys is of interest of industrial research in recent years¹, as heat transfer media in the field of nuclear-power generation. This interest was stimulated by the need to remove large quantity of heat from nuclear-power reactors at moderate coolant velocities and temperature drops. Liquid metals possess many desirable characteristics such as low vapor pressures, high thermal conductivities, high boiling points, and good thermal and reaction stability, which permit low pressure operation of coolant systems at high temperatures and radiation fluxes. The thermodynamic properties of these elements are well known as a general rule², but there are temperature regions where accurate information does not exist. The experimental data for elevated temperatures stem from the high chemical reactivity of these elements. They can really react with components of the surrounding atmosphere such as oxygen, nitrogen, carbon dioxide, and water vapor. It is difficult to obtain material of high impurity, and it is easy to contaminate samples during measurements. This is especially true for liquid alkali metals. In regarding to this reference, several equations of states³⁻⁵ and various statistical mechanical theories^{6,7} were employed to describe the thermodynamic behavior of metal alloys in addition to experimental work⁸⁻¹¹. Significant structure theory developed by Eyring *et al*¹² was used in prediction of thermodynamic properties of liquid metals and metal alloys. Equations of states predicted for metal alloys, are also helpful in describing thermodynamic properties. In present work, we have employed Flory's statistical theory to compute the thermodynamic properties of metal alloys. Excellent agreement between theoretical and experimental values is found.

THEORETICAL

Characteristic and reduced parameters of pure components are calculated according to procedure, utilizing eqs (2), (3) and (4), followed in chapter II.

Characteristic pressure of binary liquid mixtures can be expressed as,

$$P^* = \left[(\psi_1 P_1^* + \psi_2 P_2^*) - (\psi_1 \theta_2 X_{12}) \right] \quad (1)$$

In the case of binary system, interaction parameter is defined as,

$$X_{12} = P_1^* \left[1 - \left(\frac{P_2^*}{P_1^*} \right)^{1/2} \left(\frac{V_2^*}{V_1^*} \right)^{1/6} \right]^2 \quad (2)$$

and the characteristic temperatures is given by^{13,14}

$$T^* = \frac{P^*}{\frac{\psi_1 P_1^*}{T_1^*} + \frac{\psi_2 P_2^*}{T_2^*}} \quad (3)$$

The reduced temperatures

$$\tilde{T} = \frac{T}{T^*} \quad (4)$$

Ideal reduced volume and the ideal reduced temperature for a multi component system can be expressed as,

$$\tilde{V}^0 = x_1 \tilde{V}_1 + x_2 \tilde{V}_2 \quad (5)$$

The ideal reduced temperature can be written as,¹⁵

$$\tilde{T}^0 = \frac{\tilde{V}^{0^{1/3}} - 1}{\tilde{V}^{0^{1/3}}} \quad (6)$$

The excess reduced volume can be expressed^{14,15} by following relation:

$$\tilde{V}^E = \tilde{V}^{0^{1/3}} \left(\frac{4}{3} - \tilde{V}^{0^{1/3}} \right)^{-1} (\tilde{T} - \tilde{T}^0) \quad (7)$$

The reduced volume for the mixtures is given by

$$\tilde{V} = \tilde{V}^E + \tilde{V}^0 \quad (8)$$

$$V^* = \frac{V}{\tilde{V}} \quad (9)$$

The excess volume of the mixture is defined as,¹⁵

$$V^E = (x_1 V_1 + x_2 V_2) \tilde{V}^E \quad (10)$$

Thermal expansion coefficient of the mixtures is calculated by the equation

$$\alpha = \frac{3\left(\tilde{V}^{\frac{1}{3}} - 1\right)}{T\left(1 - 3\left(\tilde{V}^{\frac{1}{3}} - 1\right)\right)} \quad (11)$$

Isothermal compressibility for liquid mixtures can be computed by following expression:

$$\beta_T = \frac{\alpha T \tilde{V}^2}{P^*} \quad (12)$$

Internal pressure (P_i) can be expressed as a function of thermal expansion coefficient α and isothermal compressibility (β_T) through the relation,

$$P_i = \frac{\alpha T}{\beta_T} \quad (13)$$

$$P_i = \frac{P^*}{\tilde{V}^2} \quad (14)$$

To compute heat capacity at constant pressure and excess heat capacity following expressions have been used.

Heat capacity at constant pressure of mixtures (C_p) is defined as,

$$C_p = C_p^E + C_{p(idl)} \quad (15)$$

where $C_{p(idl)}$ is ideal heat capacity of mixture is

$$C_{p(idl)} = \sum x_i C_{pi} \quad (16)$$

C_{pi} = Heat capacity of i^{th} pure component, C_p^E is defined by Khanwalkar et al¹⁶ according to Flory theory

$$C_p^E = \frac{P^* V^*}{T^*} \left[\frac{1}{\left(\frac{4}{3} \tilde{V}^{\frac{1}{3}} - 1\right)} - \sum_i \left\{ \frac{x_i}{\left(\left(\frac{4}{3} \tilde{V}_i^{\frac{1}{3}} - 1\right)\right)} \right\} \right] \quad (17)$$

Adiabatic compressibility has been evaluated utilizing well-known thermodynamic relation

$$\beta_T - \beta_s = \frac{\alpha^2 TV}{C_p} \quad (18)$$

which in turn becomes

$$\beta_s = \beta_T - \frac{\alpha^2 TV}{C_p} \quad (19)$$

$$\beta_s = \frac{\alpha T \tilde{V}^2}{P^*} - \frac{\alpha^2 TV}{C_p} \quad (20)$$

$$\beta_s = \frac{\alpha T \tilde{V}}{P^*} \left[\tilde{V} - \frac{\tilde{\alpha}}{C_p} \right] \quad (21)$$

$$\tilde{\alpha} = \alpha T^* \quad (22)$$

$$\tilde{C}_p = \frac{C_p}{\left(\frac{P^* V^*}{T^*} \right)} \quad (23)$$

with the help of eq (21), β_s , for the mixtures can be calculated.

The heat capacities ratio (γ) and heat capacity at constant volume for the mixtures is given by relation

$$\gamma = \frac{\beta_T}{\beta_s} = \frac{C_p}{C_v} \quad (24)$$

Pseudo Grüneisen parameter (Γ) of the mixture has been evaluated using the following relation:

$$\Gamma = \frac{\gamma - 1}{\alpha T} \quad (25)$$

For the evaluation of density of mixture following simplifying expression has been taken in to account

$$\rho = \frac{M}{V} \quad (26)$$

or

$$\rho = \frac{x_1 M_1 + x_2 M_2}{(x_1 V_1^* + x_2 V_2^*) \bar{V}} \quad (27)$$

Ultrasonic velocity of mixture has been obtained with the help of following thermodynamic expression:

$$c = \left(\frac{1}{\beta_s \rho} \right)^{\frac{1}{2}} \quad (28)$$

RESULTS AND DISCUSSION

Flory's statistical theory has been employed to compute the excess molar volume (V^E), density (ρ), ultrasonic velocity (c), excess heat capacity at constant pressure (C_p^E), heat capacity at constant pressure (C_p), heat capacity at constant volume (C_v), thermal expansion coefficient (α), isothermal compressibility (β_T), adiabatic compressibility (β_S) and heat capacities ratio (γ) of metal alloys (Na + Cs and K + Rb) at three different temperatures 323.15K, 423.15K and 523.15K for entire range of composition. Experimental data required in present work have been taken from the paper of Kim and Letcher^{17,18}.

Excess molar volume (V^E), density (ρ) and ultrasonic velocity (c) have been computed employing eqs (10), (27) and (28) for which reduced and characteristic parameter of mixtures and pure components are required. These parameters are calculated utilizing different equations discussed in the theoretical section of chapter V. The experimental and theoretical values of density (ρ) and ultrasonic velocity (c) at entire range of mole fraction and temperature for alloys with percentage deviation are reported in Table-1. Careful study of this Table reveals that density smoothly decreases with increasing temperature at fixed mole fraction of the first component. At constant temperature density values decrease with increase in composition of first component in each metal alloys. Ultrasonic velocity decreases with increasing temperature whereas it increases with increasing composition of first component of each alloy at constant temperature. Measurable percentage deviation values are observed in K + Rb alloy and minimum percentage deviation in the values of ultrasonic velocity are

observed for Na + Cs alloy at all temperatures. An excellent agreement is observed between experimental and theoretical values of density. A close agreement between theoretical and experimental findings confirms the validity of present approach.

Excess heat capacity at constant pressure (C_p^E), heat capacity at constant pressure (C_p) and heat capacity at constant volume (C_v) are computed using eqs (17), (15) and (24). The experimental and theoretical values of these thermodynamic properties with percentage deviations are reported in Table -2. The heat capacities decrease with increase in temperature and composition of the first component in each metal alloy at constant temperature following the trend of experimental values of C_p and C_v . A close perusal of Table-2 shows that there is fair agreement between experiment and theoretical findings for both the alloys.

Thermal expansion coefficient (α) and isothermal compressibility (β_T) of alloys have been computed using eqs (11) and (12) respectively. The experimental and theoretical values of α and β_T along with their percentage deviation, are reported in Table-3. The theoretical values of α and β_T increase with increase in temperature and decrease continuously with increasing the composition of the first component in each alloy at constant temperature following the experimental trend mostly in all cases.

Adiabatic compressibility (β_s) and heat capacities ratio (γ) values are calculated using eqs (21) and (24) respectively. The experimental and theoretical values of β_s and γ along with the percentage deviations are reported in Table-4. Maximum percentage deviations in values of β_s for K + Rb alloy are observed whereas those of minimum deviations are observable in the case Na + Cs alloy. Deviations in the values of β_s are found to be maximum for middle composition range. Both the thermodynamic properties increase with increase in temperature at all the mole fractions. On increasing the composition of first component in the alloys, the values of β_s fluctuate and do not show a smooth variation.

Table 1. Excess volume (V^E), density (ρ) and ultrasonic velocity (u) of metal alloys at 323.15K, 423.15K and 523.15K

T=323.15K							
Na+Cs							
x_1	V^E (Theo) $\text{cm}^3\text{mol}^{-1}$	ρ (Theo) gm cm^{-3}	c (Theo) m s^{-1}	ρ (Exp) gm cm^{-3}	c (Exp) m s^{-1}	ρ %	c %
0.197	0.0021	1.3664	1270.6	1.3660	1287.0	-0.03	1.27
0.340	0.0033	1.2837	1332.7	1.2840	1319.0	0.03	-1.04
0.510	0.0036	1.1789	1419.4	1.1790	1381.0	0.01	-2.78
0.594	0.0033	1.1243	1468.6	1.1240	1417.0	-0.03	-3.64
0.710	0.0025	1.0456	1545.6	1.0460	1489.0	0.03	-3.80
0.821	0.0012	0.9666	1631.2	0.9670	1592.0	0.04	-2.46
0.862	0.0006	0.9364	1666.4	0.9370	1608.0	0.07	-3.63
0.950	-0.0008	0.8696	1750.2	0.8690	1697.0	-0.07	-3.13
K+Rb							
x_1	V^E (Theo) $\text{cm}^3\text{mol}^{-1}$	ρ (Theo) gm cm^{-3}	c (Theo) m s^{-1}	ρ (Exp) gm cm^{-3}	c (Exp) m s^{-1}	ρ %	c %
0.223	-0.3917	1.7642	1101.7	1.7500	987.0	-0.81	-11.62
0.623	0.2232	1.5076	1345.5	1.5100	1041.0	0.16	-29.26
0.723	0.2927	1.4059	1464.2	1.4300	1075.0	1.69	-36.21
0.765	0.3120	1.3554	1527.7	1.3600	1098.0	0.33	-39.14
0.870	0.3358	1.2016	1742.2	1.2100	1212.0	0.70	-43.74
0.907	0.3361	1.1350	1845.9	1.1400	1227.0	0.44	-50.44
0.927	0.3346	1.0956	1910.8	1.1100	1323.0	1.30	-44.43
0.946	0.3321	1.0556	1979.7	1.0700	1448.0	1.34	-36.72
0.958	0.3300	1.0290	2027.4	1.0400	1646.0	1.06	-23.17
0.981	0.3249	0.9747	2129.7	0.9900	1934.0	1.54	-10.12
T=423.15K							
Na+Cs							
x_1	V^E (Theo) $\text{cm}^3\text{mol}^{-1}$	ρ (Theo) gm cm^{-3}	c (Theo) m s^{-1}	ρ (Exp) gm cm^{-3}	c (Exp) m s^{-1}	ρ %	c %
0.197	0.0044	1.3288	1212.3	1.3290	1252.0	0.01	3.17
0.340	0.0060	1.2485	1272.2	1.2490	1282.0	0.04	0.77
0.510	0.0064	1.1468	1355.8	1.1460	1340.0	-0.07	-1.18
0.594	0.0059	1.0938	1403.3	1.0940	1377.0	0.02	-1.91
0.710	0.0047	1.0174	1477.5	1.0180	1448.0	0.06	-2.04
0.821	0.0028	0.9406	1560.1	0.9410	1545.0	0.04	-0.98
0.862	0.0020	0.9112	1594.1	0.9110	1562.0	-0.03	-2.06
0.950	-0.0001	0.8464	1674.9	0.8460	1657.0	-0.04	-1.08

K+Rb

x_1	V^E (Theo) $\text{cm}^3\text{mol}^{-1}$	ρ (Theo) gm cm^{-3}	c (Theo) m s^{-1}	ρ (Exp) gm cm^{-3}	c (Exp) m s^{-1}	ρ %	c %
0.223	0.2359	1.7023	992.1	1.7000	954.0	-0.14	-4.00
0.623	0.1756	1.4720	1317.4	1.4700	1015.0	-0.13	-29.80
0.723	0.1352	1.3771	1465.1	1.4000	1049.0	1.64	-39.67
0.765	0.1163	1.3295	1542.9	1.3300	1073.0	0.04	-43.79
0.870	0.0654	1.1827	1801.2	1.1800	1196.0	-0.23	-50.61
0.907	0.0469	1.1186	1924.6	1.1200	1208.0	0.12	-59.32
0.927	0.0368	1.0805	2001.5	1.0800	1354.0	-0.05	-47.82
0.946	0.0273	1.0418	2082.7	1.0400	1467.0	-0.18	-41.97
0.958	0.0213	1.0160	2138.8	1.0100	1645.0	-0.60	-30.02
0.981	0.0100	0.9632	2258.7	0.9600	1901.0	-0.33	-18.82

T=523.15K

Na+Cs

x_1	V^E (Theo) $\text{cm}^3\text{mol}^{-1}$	ρ (Theo) gm cm^{-3}	c (Theo) m s^{-1}	ρ (Exp) gm cm^{-3}	c (Exp) m s^{-1}	ρ %	c %
0.197	0.0081	1.2904	1153.5	1.2900	1217.0	-0.03	5.22
0.340	0.0804	1.2111	1203.9	1.2130	1245.0	0.16	3.30
0.510	0.0111	1.1139	1291.4	1.1140	1299.0	0.00	0.59
0.594	0.0106	1.0626	1337.1	1.0620	1337.0	-0.05	0.00
0.710	0.0090	0.9885	1408.3	0.9890	1408.0	0.05	-0.02
0.821	0.0066	0.9140	1487.6	0.9140	1498.0	0.01	0.69
0.862	0.0055	0.8855	1520.3	0.8860	1516.0	0.06	-0.28
0.950	0.0028	0.8225	1597.8	0.8220	1618.0	-0.06	1.25

K+Rb

x_1	V^E (Theo) $\text{cm}^3\text{mol}^{-1}$	ρ (Theo) gm cm^{-3}	c (Theo) m s^{-1}	ρ (Exp) gm cm^{-3}	c (Exp) m s^{-1}	ρ %	c %
0.223	0.1639	1.6508	944.0	1.6500	921.0	-0.05	-2.50
0.623	0.1880	1.4283	1257.7	1.4300	989.0	0.12	-27.17
0.723	0.1506	1.3368	1401.0	1.3600	1024.0	1.71	-36.82
0.765	0.1312	1.2909	1476.5	1.2900	1049.0	-0.07	-40.76
0.870	0.0754	1.1492	1727.8	1.1500	1179.0	0.07	-46.55
0.907	0.0540	1.0873	1847.9	1.0900	1189.0	0.25	-55.42
0.927	0.0423	1.0504	1922.8	1.0500	1341.0	-0.04	-43.39
0.946	0.0310	1.0130	2002.0	1.0100	1455.0	-0.30	-37.59
0.958	0.0239	0.9880	2056.6	0.9900	1584.0	0.20	-29.84
0.981	0.0103	0.9369	2173.4	0.9400	1868.0	0.33	-16.35

Table 2. Specific heat capacity at constant pressure and Specific heat capacity at constant volume of metal alloys at 323.15K,423.15K and523.15K

T=323.15K							
Na+Cs							
x_1	C_p^B (J mol ⁻¹ K ⁻¹)	C_p (Theo) (J mol ⁻¹ K ⁻¹)	C_v (Theo) (J mol ⁻¹ K ⁻¹)	C_p (Exp) (J mol ⁻¹ K ⁻¹)	C_v (Exp) (J mol ⁻¹ K ⁻¹)	C_p %	C_v %
0.197	0.0002	338.06	335.15	338.10	310.47	0.01	-7.95
0.340	0.0002	335.34	332.44	335.40	308.84	0.02	-7.64
0.510	0.0003	332.11	329.22	332.10	306.65	0.00	-7.36
0.594	0.0003	330.51	327.63	330.05	305.04	-0.14	-7.41
0.710	0.0002	328.31	325.44	328.30	303.42	0.00	-7.26
0.821	0.0001	326.20	323.34	326.20	300.92	0.00	-7.45
0.862	0.0001	325.42	322.56	325.40	300.46	-0.01	-7.35
0.950	-0.0001	323.75	320.89	323.70	298.62	-0.02	-7.46
K+Rb							
x_1	C_p^B (J mol ⁻¹ K ⁻¹)	C_p (Theo) (J mol ⁻¹ K ⁻¹)	C_v (Theo) (J mol ⁻¹ K ⁻¹)	C_p (Exp) (J mol ⁻¹ K ⁻¹)	C_v (Exp) (J mol ⁻¹ K ⁻¹)	C_p %	C_v %
0.223	-0.0240	347.29	344.68	347.00	321.30	-0.08	-7.28
0.623	0.0206	335.33	332.60	335.00	319.05	-0.10	-4.25
0.723	0.0308	332.34	329.58	333.00	320.19	0.20	-2.93
0.765	0.0349	331.08	328.31	331.00	318.27	-0.03	-3.15
0.870	0.0442	327.94	325.13	328.00	318.45	0.02	-2.10
0.907	0.0472	326.84	324.02	326.00	316.50	-0.26	-2.37
0.927	0.0487	326.24	323.41	326.00	316.50	-0.07	-2.18
0.946	0.0500	325.67	322.84	325.00	315.53	-0.21	-2.31
0.958	0.0509	325.31	322.48	325.00	312.50	-0.10	-3.19
0.981	0.0524	324.62	321.78	324.00	308.57	-0.19	-4.28
T=423.15K							
Na+Cs							
x_1	C_p^B (J mol ⁻¹ K ⁻¹)	C_p (Theo) (J mol ⁻¹ K ⁻¹)	C_v (Theo) (J mol ⁻¹ K ⁻¹)	C_p (Exp) (J mol ⁻¹ K ⁻¹)	C_v (Exp) (J mol ⁻¹ K ⁻¹)	C_p %	C_v %
0.197	0.0004	322.86	319.02	322.80	286.17	-0.02	-11.48
0.340	0.0006	321.01	317.19	321.00	285.84	0.00	-10.97
0.510	0.0007	318.82	315.01	318.80	285.15	-0.01	-10.47
0.594	0.0006	317.74	313.93	317.70	284.42	-0.01	-10.38
0.710	0.0005	316.24	312.45	316.20	283.08	-0.01	-10.37
0.821	0.0003	314.81	311.02	314.80	281.32	0.00	-10.56
0.862	0.0002	314.28	310.50	314.30	281.38	0.01	-10.35
0.950	0.0000	313.14	309.37	313.10	279.80	-0.01	-10.57

K+Rb

x_1	C_p^B (J mol ⁻¹ K ⁻¹)	C_p (Theo) (J mol ⁻¹ K ⁻¹)	C_v (Theo) (J mol ⁻¹ K ⁻¹)	C_p (Exp) (J mol ⁻¹ K ⁻¹)	C_v (Exp) (J mol ⁻¹ K ⁻¹)	C_p %	C_v %
0.223	0.0206	331.45	327.71	331.00	298.20	-0.13	-9.90
0.623	0.0205	321.45	317.97	321.00	300.00	-0.14	-5.99
0.723	0.0175	318.94	315.53	319.00	300.94	0.02	-4.85
0.765	0.0157	317.89	314.51	318.00	302.86	0.03	-3.85
0.870	0.0101	315.26	311.95	315.00	300.00	-0.08	-3.98
0.907	0.0076	314.33	311.04	314.00	301.92	-0.11	-3.02
0.927	0.0061	313.83	310.56	314.00	299.05	0.05	-3.85
0.946	0.0047	313.35	310.09	313.00	298.10	-0.11	-4.02
0.958	0.0037	313.05	309.80	313.00	295.28	-0.02	-4.92
0.981	0.0018	312.48	309.24	313.00	292.52	0.17	-5.71

T=523.15K

Na+Cs

x_1	C_p^B (J mol ⁻¹ K ⁻¹)	C_p (Theo) (J mol ⁻¹ K ⁻¹)	C_v (Theo) (J mol ⁻¹ K ⁻¹)	C_p (Exp) (J mol ⁻¹ K ⁻¹)	C_v (Exp) (J mol ⁻¹ K ⁻¹)	C_p %	C_v %
0.197	0.0010	310.46	305.71	310.50	264.71	0.01	-15.49
0.340	0.0103	309.43	304.65	309.40	265.81	-0.01	-14.61
0.510	0.0014	308.18	303.46	308.20	266.38	0.01	-13.92
0.594	0.0014	307.57	302.85	307.60	266.09	0.01	-13.82
0.710	0.0012	306.72	302.02	306.70	265.31	-0.01	-13.84
0.821	0.0009	305.91	301.22	305.90	264.16	0.00	-14.03
0.862	0.0008	305.61	300.92	305.60	264.59	0.00	-13.73
0.950	0.0004	304.97	300.29	305.00	262.93	0.01	-14.21

K+Rb

x_1	C_p^B (J mol ⁻¹ K ⁻¹)	C_p (Theo) (J mol ⁻¹ K ⁻¹)	C_v (Theo) (J mol ⁻¹ K ⁻¹)	C_p (Exp) (J mol ⁻¹ K ⁻¹)	C_v (Exp) (J mol ⁻¹ K ⁻¹)	C_p %	C_v %
0.223	0.0171	317.78	313.25	318.00	278.95	0.07	-12.30
0.623	0.0271	310.19	305.88	310.00	284.40	-0.06	-7.55
0.723	0.0241	308.29	304.04	308.00	285.19	-0.09	-6.61
0.765	0.0220	307.49	303.26	307.00	286.92	-0.16	-5.70
0.870	0.0145	305.48	301.32	305.00	285.05	-0.16	-5.71
0.907	0.0110	304.78	300.63	304.00	286.79	-0.26	-4.83
0.927	0.0089	304.40	300.26	304.00	284.11	-0.13	-5.68
0.946	0.0067	304.03	299.91	304.00	284.11	-0.01	-5.56
0.958	0.0053	303.80	299.69	303.00	280.56	-0.27	-6.82
0.981	0.0024	303.36	299.26	303.00	275.45	-0.12	-8.64

Table 3. Thermal expansion coefficient and Isothermal compressibility at constant volume of metal alloys at 323.15K,423.15K and523.15K

T=323.15K

Na+Cs

x_1	α (Theo) 10^3K	$\beta_T(\text{TPa}^{-1})$ (Theo)	α (Exp) 10^3K	$\beta_T(\text{TPa}^{-1})$ (Exp)	α %	β_T %
0.197	2.716	45.72	2.716	48.15	0.01	5.04
0.340	2.705	44.24	2.705	48.58	0.01	8.93
0.510	2.691	42.48	2.692	48.22	0.04	11.91
0.594	2.684	41.60	2.685	47.93	0.05	13.21
0.710	2.673	40.39	2.674	46.67	0.02	13.46
0.821	2.663	39.23	2.664	44.29	0.03	11.43
0.862	2.659	38.80	2.660	44.70	0.02	13.20
0.950	2.651	37.88	2.651	43.27	0.00	12.47

K+Rb

x_1	α (Theo) 10^3K	$\beta_T(\text{TPa}^{-1})$ (Theo)	α (Exp) 10^3K	$\beta_T(\text{TPa}^{-1})$ (Exp)	α %	β_T %
0.223	2.483	47.05	2.790	63.10	11.01	25.43
0.623	2.704	36.94	2.650	64.10	-2.03	42.37
0.723	2.744	33.45	2.600	62.90	-5.54	46.81
0.765	2.758	31.88	2.560	63.20	-7.74	49.56
0.870	2.784	27.66	2.470	58.10	-12.71	52.40
0.907	2.789	26.08	2.430	59.80	-14.79	56.38
0.927	2.791	25.22	2.410	53.30	-15.82	52.69
0.946	2.793	24.38	2.390	46.30	-16.85	47.34
0.958	2.793	23.85	2.370	37.00	-17.85	35.54
0.981	2.793	22.82	2.340	28.50	-19.37	19.93

T=423.15K

Na+Cs

x_1	α (Theo) 10^3K	$\beta_T(\text{TPa}^{-1})$ (Theo)	α (Exp) 10^3K	$\beta_T(\text{TPa}^{-1})$ (Exp)	α %	β_T %
0.197	2.861	51.82	2.862	54.19	0.04	4.37
0.340	2.848	50.09	2.849	54.71	0.03	8.45
0.510	2.833	48.01	2.834	54.36	0.05	11.67
0.594	2.825	46.99	2.826	53.84	0.05	12.73
0.710	2.813	45.57	2.814	52.33	0.04	12.92
0.821	2.802	44.21	2.803	49.88	0.05	11.36
0.862	2.797	43.71	2.798	50.22	0.03	12.96
0.950	2.788	42.63	2.788	48.17	0.01	11.49

K+Rb

x_1	α (Theo)	$\beta_T(\text{TPa}^{-1})$ (Theo)	α (Exp)	$\beta_T(\text{TPa}^{-1})$ (Exp)	α	β_T
	10^3K		10^3K		%	%
0.223	2.892	60.36	2.910	71.50	0.61	15.58
0.623	2.725	39.57	2.770	70.60	1.64	43.95
0.723	2.664	34.19	2.730	69.00	2.40	50.44
0.765	2.636	31.94	2.680	69.00	1.63	53.71
0.870	2.557	26.34	2.600	62.10	1.64	57.59
0.907	2.526	24.39	2.560	64.00	1.31	61.89
0.927	2.509	23.35	2.530	53.10	0.83	56.03
0.946	2.492	22.36	2.510	47.00	0.73	52.42
0.958	2.481	21.74	2.490	38.80	0.38	43.97
0.981	2.459	20.56	2.460	30.90	0.06	33.45

T=523.15K

Na+Cs

x_1	α (Theo)	$\beta_T(\text{TPa}^{-1})$ (Theo)	α (Exp)	$\beta_T(\text{TPa}^{-1})$ (Exp)	α	β_T
	10^3K		10^3K		%	%
0.197	3.013	59.15	3.014	61.38	0.02	3.64
0.340	3.032	57.86	3.001	61.99	-1.02	6.66
0.510	2.981	54.67	2.983	61.64	0.06	11.31
0.594	2.972	53.46	2.974	60.84	0.06	12.13
0.710	2.959	51.80	2.961	58.99	0.07	12.19
0.821	2.946	50.21	2.947	56.48	0.04	11.10
0.862	2.941	49.62	2.942	56.73	0.03	12.53
0.950	2.930	48.36	2.931	53.90	0.03	10.27

K+Rb

x_1	α (Theo)	$\beta_T(\text{TPa}^{-1})$ (Theo)	α (Exp)	$\beta_T(\text{TPa}^{-1})$ (Exp)	α	β_T
	10^3K		10^3K		%	%
0.223	3.016	68.95	3.060	81.30	1.45	15.19
0.623	2.863	44.88	3.020	78.00	5.21	42.46
0.723	2.803	38.64	2.880	76.00	2.67	49.15
0.765	2.775	36.03	2.840	75.50	2.30	52.28
0.870	2.694	29.55	2.800	66.70	3.80	55.70
0.907	2.661	27.31	2.720	68.80	2.16	60.31
0.927	2.643	26.10	2.680	56.50	1.38	53.80
0.946	2.625	24.97	2.660	50.00	1.32	50.06
0.958	2.613	24.26	2.640	43.70	1.02	44.49
0.981	2.590	22.91	2.630	33.70	1.52	32.03

Table 4. Adiabatic compressibility (β_s) and Specific heat capacity ratio (γ) at constant volume of metal alloys at 323.15K, 423.15K and 523.15K

T=323.15K						
Na+Cs						
x_1	γ (Theo)	$\beta_s(\text{Tpa}^{-1})$ (Theo)	γ (Exp)	$\beta_s(\text{Tpa}^{-1})$ (Exp)	γ %	β_s %
0.197	1.009	45.33	1.089	42.05	7.37	-7.80
0.340	1.009	43.86	1.086	40.81	7.12	-7.47
0.510	1.009	42.11	1.083	39.21	6.85	-7.39
0.594	1.009	41.24	1.082	38.39	6.77	-7.42
0.710	1.009	40.04	1.082	37.21	6.76	-7.59
0.821	1.009	38.88	1.084	36.01	6.93	-7.98
0.862	1.009	38.46	1.083	35.55	6.84	-8.18
0.950	1.009	37.54	1.084	34.54	6.93	-8.69

K+Rb						
x_1	γ (Theo)	$\beta_s(\text{Tpa}^{-1})$ (Theo)	γ (Exp)	$\beta_s(\text{Tpa}^{-1})$ (Exp)	γ %	β_s %
0.223	1.008	46.70	1.080	58.60	6.71	20.31
0.623	1.008	36.64	1.050	61.20	3.98	40.14
0.723	1.008	33.18	1.040	60.40	3.04	45.07
0.765	1.008	31.61	1.040	60.90	3.03	48.10
0.870	1.009	27.42	1.030	56.20	2.07	51.21
0.907	1.009	25.86	1.030	58.10	2.07	55.49
0.927	1.009	25.00	1.030	51.70	2.06	51.65
0.946	1.009	24.17	1.030	44.70	2.06	45.93
0.958	1.009	23.64	1.040	35.50	3.00	33.40
0.981	1.009	22.62	1.050	27.10	3.92	16.53

T=423.15K						
Na+Cs						
x_1	γ (Theo)	$\beta_s(\text{Tpa}^{-1})$ (Theo)	γ (Exp)	$\beta_s(\text{Tpa}^{-1})$ (Exp)	γ %	β_s %
0.197	1.012	51.21	1.128	45.99	10.28	-11.35
0.340	1.012	49.49	1.123	44.60	9.88	-10.96
0.510	1.012	47.44	1.118	42.82	9.47	-10.79
0.594	1.012	46.43	1.117	41.91	9.39	-10.77
0.710	1.012	45.02	1.117	40.59	9.39	-10.92
0.821	1.012	43.68	1.119	39.25	9.55	-11.29
0.862	1.012	43.18	1.117	38.74	9.38	-11.47
0.950	1.012	42.12	1.119	37.61	9.54	-11.99

K+Rb

x_1	γ (Theo)	$\beta_s(\text{Tpa}^{-1})$ (Theo)	γ (Exp)	$\beta_s(\text{Tpa}^{-1})$ (Exp)	γ %	β_s %
0.223	1.011	59.68	1.110	64.60	8.88	7.62
0.623	1.011	39.14	1.070	66.10	5.52	40.78
0.723	1.011	33.83	1.060	65.10	4.64	48.04
0.765	1.011	31.60	1.050	65.40	3.74	51.69
0.870	1.011	26.06	1.050	59.30	3.75	56.05
0.907	1.011	24.13	1.040	61.40	2.83	60.69
0.927	1.011	23.10	1.050	50.60	3.76	54.34
0.946	1.011	22.13	1.050	44.70	3.76	50.50
0.958	1.011	21.52	1.060	36.50	4.67	41.05
0.981	1.010	20.35	1.070	28.70	5.56	29.09

T=523.15K

Na+Cs

x_1	γ (Theo)	$\beta_s(\text{Tpa}^{-1})$ (Theo)	γ (Exp)	$\beta_s(\text{Tpa}^{-1})$ (Exp)	γ %	β_s %
0.197	1.016	58.24	1.173	50.48	13.42	-15.37
0.340	1.016	56.97	1.164	48.92	12.74	-16.45
0.510	1.016	53.83	1.157	46.93	12.23	-14.70
0.594	1.016	52.64	1.156	45.90	12.15	-14.69
0.710	1.016	51.01	1.156	44.42	12.15	-14.83
0.821	1.016	49.44	1.158	42.92	12.30	-15.19
0.862	1.016	48.86	1.155	42.35	12.07	-15.38
0.950	1.016	47.62	1.160	41.08	12.45	-15.92

K+Rb

x_1	γ (Theo)	$\beta_s(\text{Tpa}^{-1})$ (Theo)	γ (Exp)	$\beta_s(\text{Tpa}^{-1})$ (Exp)	γ %	β_s %
0.223	1.014	67.97	1.140	71.50	11.01	4.94
0.623	1.014	44.26	1.090	71.70	6.96	38.27
0.723	1.014	38.11	1.080	70.30	6.11	45.79
0.765	1.014	35.53	1.070	70.50	5.24	49.60
0.870	1.014	29.15	1.070	62.50	5.25	53.36
0.907	1.014	26.93	1.060	65.00	4.36	58.56
0.927	1.014	25.75	1.070	52.90	5.26	51.33
0.946	1.014	24.63	1.070	46.60	5.26	47.14
0.958	1.014	23.93	1.080	40.40	6.14	40.77
0.981	1.014	22.60	1.100	30.50	7.85	25.91

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CHAPTER-VII

**THERMAL EXPANSION
COEFFICIENT, EXCESS MOLAR
POLARIZATION, CHANGE IN
MOLAR REFRACTION, CHANGE IN
REFRACTIVE INDEX AND
CHANGE IN DIELECTRIC
CONSTANT OF BINARY LIQUID
MIXTURES**

INTRODUCTION

Experimental measurements of refractive index and dielectric constant of liquid mixtures have gained much importance during recent past¹⁻⁹. The measurements were made mostly in binary mixtures⁶⁻¹². Dielectric constant for few ternary systems has also been reported³⁻⁴. Comparatively refractive index studies of a number of binary liquid mixtures^{1,2,6,7,10,12} some ternary mixtures^{12,13} and very few quaternary systems^{14,15} have been reported earlier. Refractive index data were analyzed in terms of various mixing rules suggested by different workers from time to time¹³⁻¹⁶. However, less attention has been drawn to study the dielectric constant theoretically in the case of liquid mixtures. In order to study the interactions in various kinds of liquid mixtures using the experimental values of refractive index and dielectric constant, we are presenting here an entirely different approach. We have made an attempt here to compute the deviations in refractive indices, molar refraction, dielectric constant and molar polarization from the experimental values of refractive index and dielectric constant. In the case of refractive index studies, we have employed various theoretical mixing rules and compared the resulting values with experimental observations and rms values are obtained. In addition, an attempt has also been made to evaluate theoretically the values of thermal expansivity of liquid mixtures, namely, methyl-3-ketobutanoate + methanol (VII), methyl-3-ketobutanoate + ethanol (VII) and methyl-3-ketobutanoate + hexanol (VIII) using temperature dependent refractive indices data. Such data are available only for these mixtures⁵. For rest of the systems I-VI, temperature dependent refractive index data are not available. Hence, it has not been possible to evaluate thermal expansion coefficients of these mixtures. The results are compared with the experimental findings. The experimental values of dielectric constant, refractive index and density of six binary mixtures were taken from the recent work of Hahn, Sevejda and Dallos⁹.

THEORETICAL

Several empirical relations¹⁶ have been used to compute refractive index of binary and multi component liquid system using refractive index of pure components and density of pure components and binary systems. In the present work, we have

utilized Heller (He), Gladston-Dale (G-D), Lorentz-Lorenz (L-L), Argo-Biot (A-B), Wiener (Wi), Eykman (Eyk), Oster (Os) relations¹⁶ to compute refractive indices of systems under the present study.

The molar refraction, R_m , is obtained from Lorentz-Lorenz equation²

$$R_m = \left\{ \frac{n^2 - 1}{n^2 + 2} \right\} V_m \quad (1)$$

where n is the refractive index of mixture.

Molar polarization, $R_{m,}$ of the mixture is obtained from equation⁶

$$P_m = \left\{ \frac{(1-x)M_1 + xM_2}{\rho} \right\} \left(\frac{\epsilon_r - 1}{\epsilon_r + 2} \right) \quad (2)$$

In order to study the interactions in binary mixtures, deviations in the values of refractive index, dielectric constant, molar refraction and molar polarization have been calculated. These deviations are given by the general expression

$$\Delta Z = Z_{mix} - \sum x_i Z_i \quad (3)$$

where Z represents one of the above mentioned properties of mixture and Z_i the corresponding property of the pure component 'i'. The isobaric thermal expansivity of pure components of liquid mixtures is obtained from the following relations¹⁶:

$$\alpha_{(B)*} = - \frac{(n^2 + 0.8n + 1)}{(n^2 - 1)(n + 0.4)} \left(\frac{dn}{dT} \right) \quad (4)$$

$$\alpha_{L-L} = - \frac{6n}{(n^2 - 1)(n^2 + 2)} \left(\frac{dn}{dT} \right) \quad (5)$$

It is observed that these values are some what in agreement with those obtained using the relation proposed by Pandey *et al*^{17,18}, which is given by

$$\alpha = \frac{75.6 \times 10^{-3}}{T^{\frac{4}{3}} c^{\frac{1}{3}} \rho^{\frac{1}{3}}} \quad (6)$$

Isobaric thermal expansivity, α_m , of the mixture can be expressed as¹⁶,

$$\alpha_m = \frac{\rho_m}{\sum M_i x_i} \left[\sum_i \left(\frac{M_i}{\rho_i} \right) x_i \alpha_i + \left(\frac{\partial V^E}{\partial T} \right)_{P, X} \right] \quad (7)$$

In order to evaluate, α_m , by employing eq.(7), required parameters namely V_m and V^E are evaluated using density data. Results obtained are compared with the values of α_m , obtained from equation (6) using experimental values of sound velocity and density of binary liquid systems.

RESULTS AND DISCUSSION

In the present chapter refractive index (n), changes in refractive index (Δn), molar refraction (ΔR), dielectric constant ($\Delta \epsilon$) and excess molar polarization (ΔP or P^E) of six binary mixtures, namely, 1,2-dichloroethane + *n*-heptane (I), 1,2-dichloroethane + *n*-decane (II), 1,2-dichloroethane + *n*-dodecane (III), 1,2-dichloroethane + *n*-tetradecane (IV), 1,2-dichloroethane + *n*-hexadecane (V) and 1,2-dichloroethane + 2,2,4-trimethylpentane (VI) have been computed at 293.15K and 313.15K over the entire composition range using well-established relations. The values of isobaric thermal expansivity (α) of three binary mixture, namely, methyl-3-ketobutanoate + methanol (VII), methyl-3-ketobutanoate + ethanol (VIII) and methyl-3-ketobutanoate + hexanol (IX) have also been computed using eq (7), and compared with the experimental values obtained from eq (6) with the help of experimental data of sound velocity and density measured by Aminabhavi *et al*⁵. In preceding this work, desired experimental values of pure components and binary systems have been taken from the literature⁹. Changes in the above-mentioned properties, except α , of binary mixtures under consideration have been computed by eq (3) using experimental data of pure components.

In order to evaluate refractive indices (n) of binary liquid mixtures, several models have been used to derive mixing rules namely, Heller (He), Gladstone-Dale (G-D), Lorentz-Lorenz (L-L), Arago-Biot (A-B), Wiener (W), Eykmann (Eyk), and Oster (Os) equations. The root mean square deviations (rms) of the experimental values from the calculated values from mixing rules are reported in Table-1. Due to different nature and molecular size of contributing components significantly, a particular mixing rule provides excellent agreement at some places and deviates at other. Order of validity of the above mentioned mixing rules has generally the following sequence in binary systems under investigation.

$$\text{Eyk} > \text{G-D} > \text{Os} > \text{L-L} > \text{W} > \text{A-B} > \text{H}$$

Changes in molar refraction, ΔR , have been calculated using eq (3) for which the values of molar refraction of pure components and binary systems have been computed using eq (1). Experimental values of ΔR were calculated using experimental values of refractive index and density of binary systems. Theoretical evaluation of refractive index of binary mixtures has been carried out using refractive index and density data of pure components with the help of all the abovementioned mixing rules. With the help of experimental data and theoretically evaluated refractive index values, changes in molar refraction have also been computed. Graphs between theoretical and experimental values of ΔR against mole fraction have been plotted for all the systems under investigation at temperatures 293.15 K and 313.15 K. A comparative study of computed ΔR values at different concentrations using entirely different methods have been shown in figs 1 (a) to 1(l). There is close agreement between experimental and theoretical values of ΔR obtained by Eyk, Os and G-D relations. The values of ΔR obtained by Eykmann relation coincide with the experimental values of ΔR at temperatures 293.15 K and 313.15 K for all the binary systems under consideration. For all the systems only positive values of ΔR are observed and these values are found larger at higher temperature. Graphical trends of figs-1(a) to 1(l) is identical to that of excess molar volume employed to explain interaction effects in binary systems under present study⁹. On this basis several conclusions can be drawn. Mixing with the non-polar alkanes reduces the strong intermolecular interactions between the polar gauche conformers in pure 1,2- dichloroethane, and the equilibrium of 1,2 dichloroethane is shifted towards the non-polar trans conformer. Both effects lead to the observed large positive values of changes in molar refraction. Larger the values of ΔR and temperature, smaller will be the molecular interactions. A careful study of nature of curves (figs-1) shows that values of ΔR depend on temperature. Since ΔR values depend upon molecular structure of components of binary systems. Such behavior may be attributed mainly to the association with polar character of 1,2 dichloroethane. From the above discussion, it can be concluded that interactions depend on temperature and relative amounts of pure components in binary systems. Excess molar volume is a thermodynamic properties employed to study molecular interactions. In the similar

manner, ΔR values also explain the nature of intermolecular interactions in the systems under consideration.

The values of molar polarization of pure components and binary systems were calculated by eq (2). With the help of P_{mix} , P_1 and P_2 , excess molar polarization (P^E) of binary liquid mixtures have been computed using generalized eq (3). The values of P^E for six binary systems are plotted against the mole fraction and are shown in figs-2(a) and 2(b) at temperatures 293.15 K and 313.15 K respectively. As temperature increases intermolecular interaction decreases and the values of excess molar polarization also decrease. Larger the negative values of P^E , larger will be the interaction between components of the binary systems and vice versa.

Dielectric constant plays an important role in the arrangement of molecules and in the local structures of liquids. The changes in the dielectric constant ($\Delta\epsilon$) have been evaluated with the help of eq (3) using experimental data of pure components and binary systems. This reflects the extent of interactions between 1,2 dichloromethane and n-alkanes. Furthermore, the values of $\Delta\epsilon$ have been plotted at each investigated temperatures in binary domain $[x_1x_2]$, and results at 293.15K and 313.15K are displayed in figs-3(a) and 3(b). For all the binaries investigated, $\Delta\epsilon$ values are always negative over the entire composition range. The absolute values of $\Delta\epsilon$ extremely increase as chain length of n-alkanes increases. In general, literature survey it has been observed that for $\Delta\epsilon < -1.51$, strong interactions occur between the binary components. Keeping this view in mind it is seen that there exists nearly strong interactions between the binary components especially in system (V) than others systems at both the temperatures. The influence of temperature on the values of $\Delta\epsilon$, for the binary system is significant. Strong interactions occur at low temperature and comparatively weak interactions at higher temperature at identical mole fraction. These conclusions are drawn from figs-3(a) and (3b). From above discussion, it can be concluded that the relative strength of specific intermolecular interactions between 1,2-dichloroethane and higher order alkanes decreases as the alkane-carbon chain length increases. A better assessment of these interactions could be obtained by heat of mixing measurements.

The changes of refractive indices on mixing vs. mole fractions are plotted and shown in figs-4(a) and 4(b) at temperatures 293.15 K and 313.15 K for all the binary systems under consideration. The values of Δn are negative at all the mole fractions and both the temperatures as evident from figures. It is observed that the graphical trend of Δn is identical to that of ΔP and $\Delta \epsilon$. On this basis we conclude that Δn can also be used to explain specific molecular interactions between the components of binary systems in similar manner as shown by ΔP and $\Delta \epsilon$ at temperatures 293.15 K and 313.15 K over entire mole fraction range.

Isobaric thermal expansivity, α , of three binary systems have been studied at three temperatures 298.15 K, 303.15 K and 308.15 K. The values of α of pure components have been evaluated from Eykman and Lorentz-Lorenz relations using refractive indices values of pure components at varying temperatures. With the help of values of α , ρ , $\left(\frac{\partial V^E}{\partial T}\right)$, and ρ_m , eq (7) has been employed to compute isobaric thermal expansivity of binary mixtures. Experimental values of α have been computed by employing eq (6) using experimental values of ultrasonic velocity and density. The values of isobaric thermal expansivity increase with increase in temperature at constant mole fraction. Experimental and theoretical values along with the percentage deviations are reported in Table-2. A comparative study shows that Eykman relation provides better results than Lorentz-Lorenz relation for all the systems under the present investigation.

Fig 1. A comparison between experimental and theoretical values of change in molar refraction (ΔR) with mole fraction (x_1) at 293.15K and 313.15K

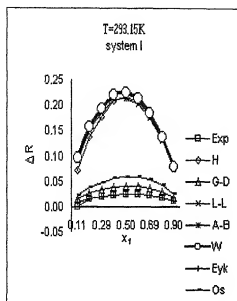


Fig. 1.(a)

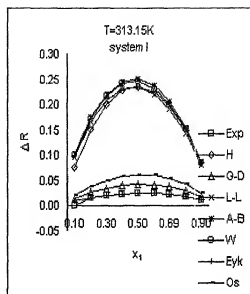


Fig. 1.(g)

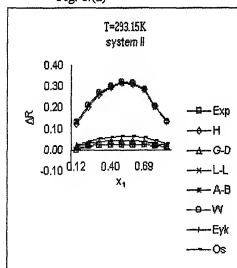


Fig 1(b)

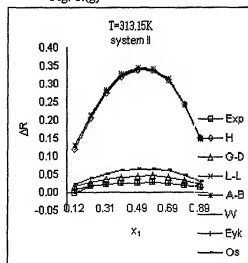


Fig 1(h)

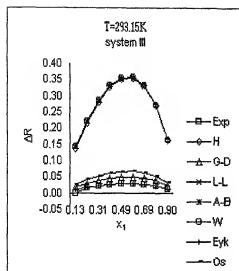


Fig. 1.(c)

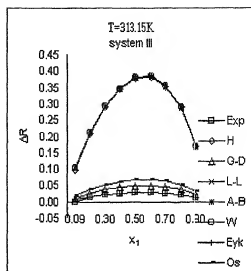


Fig. 1.(i)

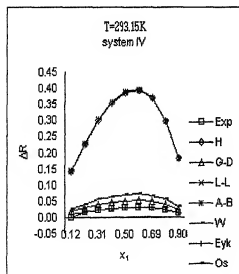


Fig. 1.(d)

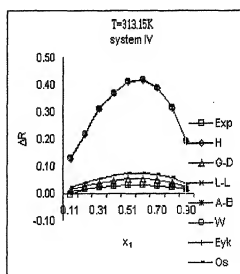


Fig. 1.(j)

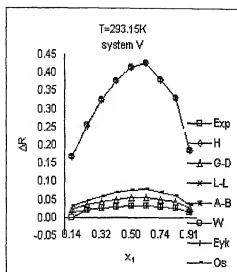


Fig. 1.(e)

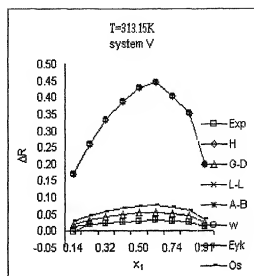


Fig. 1.(k)

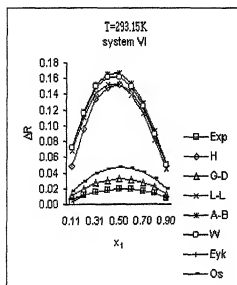


Fig. 1.(f)

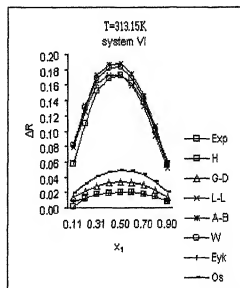


Fig. 1.(l)

Fig .2. Excess molar polarization (P^E) vs. mole fraction (x_1) of systems mentioned in table-1 at 293.15K and 313.15K

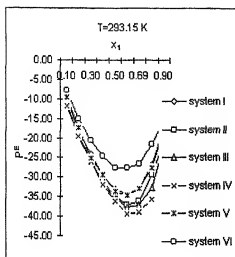


Fig .2(a)

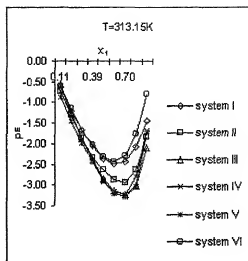


Fig .2(b)

Fig .3. Change in dielectric constant ($\Delta\epsilon$) vs. mole fraction (x_1) of systems mentioned in table-1 at 293.15K and 313.15K

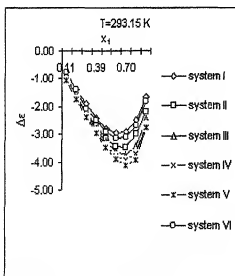


Fig .3(a)

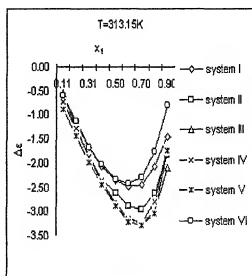


Fig .3(b)

Fig. 4. Change in dielectric constant (Δn) vs. mole fraction (x_1) of systems mentioned in table-I at 293.15 K and 313.15 K

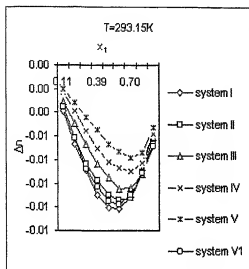


Fig. 4(a)

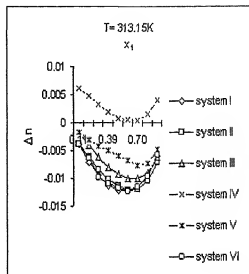


Fig. 4(b)

Table 1.

Root-mean-square deviations of the experimental values from the calculated values using the Heller (He), Dale-Gladston (G-D), Lorentz-Lorenz (L-L), Argo-Biot (A-B), Wiener (Wi), Eykman (Eyk), Oster (Os).

T=293.15K

Systems	H	G-D	L-L	A-B	W	Eyk	Os
1,2 dichloroethane+n-heptane	0.09	0.02	0.09	0.09	0.09	0.01	0.02
1,2 dichloroethane+n-dccane	0.09	0.01	0.09	0.09	0.09	0.01	0.01
1,2 dichloroethane+n-dodecane	0.09	0.01	0.93	0.09	0.09	0.01	0.01
1,2 dichloroethane+n-tetradecane	0.10	0.01	0.10	0.10	0.10	0.01	0.01
1,2 dichloroethane+n-hexadecane	0.10	0.01	0.10	0.10	0.10	0.01	0.02
1,2 dichloroethane+2,2,4-trimethylpentane	0.05	0.03	0.04	0.04	0.04	0.03	0.03

T=313.15K

Systems	H	G-D	L-L	A-B	W	Eyk	Os
1,2 dichloroethane+n-heptane	0.09	0.01	0.08	0.09	0.08	0.01	0.01
1,2 dichloroethane+n-dccane	0.10	0.01	0.10	0.10	0.10	0.00	0.01
1,2 dichloroethane+n-dodecane	0.11	0.01	0.11	0.11	0.11	0.01	0.01
1,2 dichloroethane+n-tetradecane	0.11	0.02	0.11	0.11	0.11	0.02	0.02
1,2 dichloroethane+n-hexadecane	0.10	0.02	0.10	0.10	0.10	0.02	0.02
1,2 dichloroethane+2,2,4-trimethylpentane	0.06	0.03	0.05	0.06	0.06	0.03	0.03

Table 2. Thermal expansion coefficient of binary liquid mixtures using refractive index

Methyl-3-Ketobutanoate(1) + Methanol(2)

T=298.15K

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (L-L)	$\alpha \times 10^3 K$ (Eyk)	% dev (L-L)	% dev (Eyk)
0.1017	1.236	1.087	1.144	12.05	7.50
0.1887	1.195	1.042	1.102	12.85	7.84
0.4048	1.128	1.040	1.106	7.85	1.96
0.5038	1.107	1.052	1.121	4.97	-1.23
0.6056	1.090	1.045	1.116	4.12	-2.33
0.7015	1.078	1.009	1.081	6.35	-0.31
0.8024	1.068	1.022	1.095	4.29	-2.55
0.8994	1.059	1.011	1.086	4.47	-2.54

T=303.15K

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (L-L)	$\alpha \times 10^3 K$ (EyK)	% dev (L-L)	% dev (EyK)
0.1017	1.247	1.097	1.153	11.99	7.51
0.1887	1.205	1.052	1.111	12.74	7.79
0.4048	1.137	1.049	1.115	7.72	1.90
0.5038	1.117	1.061	1.129	5.05	-1.06
0.6056	1.100	1.053	1.123	4.27	-2.1
0.7015	1.087	1.017	1.088	6.45	-0.13
0.8024	1.076	1.029	1.102	4.39	-2.37
0.8994	1.068	1.018	1.092	4.67	-2.24

T=308.15K

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (L-L)	$\alpha \times 10^3 K$ (EyK)	% dev (L-L)	% dev (EyK)
0.1017	1.255	1.105	1.161	11.95	7.52
0.1887	1.214	1.060	1.119	12.67	7.78
0.4048	1.145	1.056	1.122	7.77	2.03
0.5038	1.124	1.068	1.136	5.03	-1.01
0.6056	1.109	1.061	1.130	4.27	-2.03
0.7015	1.095	1.024	1.096	6.43	-0.06
0.8024	1.085	1.036	1.109	4.51	-2.16
0.8994	1.077	1.026	1.099	4.76	-2.07

Methyl-3-Ketobutanoate(1) + Ethanol(2)

T=298.15K

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (L-L)	$\alpha \times 10^3 K$ (EyK)	% dev (L-L)	% dev (EyK)
0.1051	1.236	1.144	1.210	7.48	2.14
0.2040	1.202	1.169	1.238	2.71	-2.95
0.3085	1.167	1.159	1.229	0.69	-5.28
0.4046	1.145	1.152	1.223	-0.67	-6.85
0.5056	1.124	1.144	1.217	-1.81	-8.20
0.6070	1.101	1.117	1.190	-1.47	-8.08
0.7033	1.089	1.074	1.147	1.46	-5.28
0.8022	1.041	1.144	1.225	-9.91	-17.7
0.9020	1.066	1.038	1.112	2.64	-4.37

T=303.15K

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (L-L)	$\alpha \times 10^3 K$ (EyK)	% dev (L-L)	% dev (EyK)
0.1051	1.248	1.153	1.218	7.65	2.40
0.2040	1.212	1.177	1.245	2.91	-2.66
0.3085	1.177	1.167	1.236	0.91	-4.98
0.4046	1.154	1.159	1.230	-0.47	-6.57
0.5056	1.134	1.152	1.224	-1.53	-7.83
0.6070	1.112	1.124	1.197	-1.08	-7.59
0.7033	1.099	1.081	1.154	1.69	-4.95
0.8022	1.084	1.051	1.124	3.09	-3.71
0.9020	1.073	1.044	1.118	2.70	-4.22

T=308.15K

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (L-L)	$\alpha \times 10^3 K$ (EyK)	% dev (L-L)	% dev (EyK)
0.1051	1.261	1.158	1.223	8.18	3.00
0.2040	1.223	1.182	1.250	3.29	-2.21
0.3085	1.189	1.172	1.241	1.40	-4.41
0.4046	1.166	1.165	1.235	0.03	-5.99
0.5056	1.144	1.158	1.229	-1.14	-7.35
0.6070	1.121	1.130	1.202	-0.85	-7.28
0.7033	1.108	1.087	1.160	1.88	-4.69
0.8022	1.094	1.057	1.131	3.34	-3.36
0.9020	1.083	1.051	1.125	2.93	-3.90

Methyl-3-Ketobutanoate(1) + 1-hexanol(2)

T=298.15K

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (L-L)	$\alpha \times 10^3 K$ (EyK)	% dev (L-L)	% dev (EyK)
0.1036	1.180	1.063	1.140	9.91	3.40
0.204	1.171	1.077	1.154	8.00	1.43
0.3064	1.159	1.099	1.176	5.18	-1.47
0.4075	1.147	1.082	1.159	5.70	-1.01
0.5096	1.135	1.108	1.185	2.33	-4.46
0.6081	1.121	1.085	1.162	3.21	-3.63
0.7063	1.105	1.128	1.204	-2.07	-9.00
0.806	1.089	1.062	1.138	2.39	-4.61
0.9023	1.074	1.040	1.116	3.10	-3.96

T=303.15K

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (L-L)	$\alpha \times 10^3 K$ (EyK)	% dev (L-L)	% dev (EyK)
0.1036	1.189	1.069	1.146	10.08	3.65
0.204	1.181	1.083	1.159	8.28	1.79
0.3064	1.170	1.104	1.181	5.58	-0.98
0.4075	1.157	1.088	1.165	5.93	-0.71
0.5096	1.143	1.114	1.190	2.60	-4.10
0.6081	1.129	1.091	1.168	3.34	-3.43
0.7063	1.115	1.133	1.209	-1.62	-8.46
0.806	1.098	1.068	1.144	2.70	-4.21
0.9023	1.081	1.047	1.122	3.20	-3.77

T=308.15K

x_1	$\alpha \times 10^3 K$ (Exp)	$\alpha \times 10^3 K$ (L-L)	$\alpha \times 10^3 K$ (EyK)	% dev (L-L)	% dev (EyK)
0.1036	1.200	1.077	1.153	10.24	3.90
0.204	1.190	1.091	1.167	8.35	1.95
0.3064	1.179	1.112	1.188	5.68	0.78
0.4075	1.167	1.095	1.172	6.12	-0.42
0.5096	1.155	1.121	1.197	2.92	-3.68
0.6081	1.140	1.099	1.175	3.59	-3.08
0.7063	1.124	1.139	1.216	-1.46	-8.20
0.806	1.108	1.076	1.151	2.94	-3.87
0.9023	1.091	1.054	1.129	3.40	-3.48

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CHAPTER - VIII

STUDIES OF ACOUSTIC NON- LINEAR BEHAVIOR OF BINARY AND MULTICOMPONENT SYSTEMS

INTRODUCTION

Acoustic non linear effects occur due to greater attenuation of the high frequency components in comparison to low frequency ones when sound waves of high intensity are allowed to propagate in liquids. The deviation from linearity in the propagation process is symbolized by the factor (B/A) , called the non-linearity parameter. It is the ratio of the coefficients of the quadratic to linear terms of a Taylor series used to express the equation of state of the medium in terms of pressure and density. From the knowledge of this parameter, internal pressure, intermolecular spacing, acoustic scattering and structural behavior can be studied. Further experimental study on this subject reveals that the non-linear interaction of two parallel sound beams could produce scattering. It is found that scattering does not take place when the incident beams are orthogonal. Beyer *et al*¹⁻⁴ were the first who presented the theoretical formalism of non-linearity parameter and determined it for a number of organic liquids using sound velocity and other thermodynamic data. Hartmann *et al*⁵ discussed non-linear behaviour of liquids in the view of the potential by assuming volume dependence of sound velocity. An attempt made by Endo⁶ shows that non-linearity parameter is a polynomial of heat capacity, and can be computed from thermodynamic coefficient of sound velocity on the basis of thermodynamic consideration. Hartmann and Balizer⁵ have determined the values of non-linearity parameter for *n* alkane using a new equation of state. Several workers⁷⁻⁹ have carried out theoretical evaluation of this parameter for various classes of liquids. It has become very interesting to predict the extent of interactions, which are due to deviation from linearity in ordinary acoustics. Beyer^{1, 2}, Nomoto^{1-4, 10}, Nomoto¹¹, Kor *et al*¹²⁻¹⁵, Pandey *et al*^{16, 17} and Sharma¹⁸⁻²¹ succeeded in computing non linearity parameter (B/A) for a number of liquids using thermodynamic approach. B/A plays a significant role in non-linear acoustics as well as underwater acoustics. Tong *et al*²² proposed a simplified method for the calculation of B/A values for liquids making use of Schaaffs²³ equation of sound velocity. Recently, Jugan *et al*²⁴ used this method for calculating B/A values of binary liquid mixture. In the present work, non-linearity parameter has been computed using thermodynamic method, Hartmann method based on potential parameter and an empirical relation. A comparison of B/A values obtained from three methods has been made in order to review above-mentioned approaches.

THEORETICAL

Ultrasonic velocity in liquids is affected by intermolecular interaction. The primary assumption made is that the intermolecular potential energy is the dominant factor in determining sound speed in liquids. It can be shown that the thermal pressure contribution to the sound speed is negligible in comparison to the internal pressure contribution. This approach approximately predicts qualitatively accurate results, and justifies the physical basis for the measured sound velocity. Under these assumptions Hartmann⁵ theoretically derived expression for B/A as,

$$B/A = 2 + \frac{(0.98 \times 10^4)}{c} \quad (1)$$

where c is in ms^{-1}

For justification of this expression B/A values, evaluated for organic liquids, water, liquid metals by Beyer, have been compared with that obtained from Ballou's empirical rule. Ballou's empirical relation for organic liquids can be expressed as,⁵

$$B/A = -0.5 + \frac{(1.2 \times 10^4)}{c} \quad (2)$$

where c is in ms^{-1}

Thermal expansion coefficient and isothermal compressibility values are computed using the following relations:^{25, 26}

$$\alpha = \frac{75.6 \times 10^{-3}}{T^{\frac{1}{3}} c^{\frac{1}{2}} \rho^{\frac{1}{3}}} \quad (3)$$

and

$$\beta_s = \frac{1}{c^2 \rho} \quad (4)$$

$$\beta_T = \frac{1.71 \times 10^{-3}}{T^{\frac{4}{9}} c^{\frac{1}{2}} \rho^{\frac{4}{3}}} \quad (5)$$

$$\frac{\beta_T}{\beta_S} = \gamma \quad (6)$$

In the present work, two aforementioned expressions for B/A have been extended to binary and multicomponent systems and results have been compared with the values of B/A obtained by a thermodynamic method developed by Tong and Dong.

The non-linearity parameter (B/A) for liquid is obtained from the isentropic equation of state in which the pressure (P) is expanded in a Taylor's series about its equilibrium value in terms of density ρ

$$P = P_o + A \left(\frac{\rho - \rho_o}{\rho} \right) + \frac{B}{2} \left(\frac{\rho - \rho_o}{\rho} \right)^2 + \dots \quad (7)$$

where subscript "o" denotes the equilibrium value. The ratio B/A in this equation is called the acoustic non-linearity parameter B/A. The coefficients A and B are defined as,

$$A = \rho_o \left[\left(\frac{\partial P}{\partial \rho} \right)_s \right]_{\rho=\rho_o} \quad (8)$$

$$B = \rho_o^2 \left[\left(\frac{\partial^2 P}{\partial \rho^2} \right)_s \right]_{\rho=\rho_o} \quad (9)$$

Since

$$c_o = \left[\left(\frac{\partial P}{\partial \rho} \right)_s \right]_{\rho=\rho_o} \quad (10)$$

at equilibrium

$$B/A = \rho \left[\left(\frac{\partial c^2}{\partial P} \right)_s \right] \quad (11)$$

From this expression it is observed that B/A is related to sound velocity.

Tong *et al*²² applied Schaaffs equation²³ for sound velocity in the basic equation of B/A . Schaaffs proposed that the sound velocity in organic liquids is related to the molecular structure and proposed that van der Waals equation could be applied to all organic liquids at room temperatures and under atmospheric pressures.

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \quad (12)$$

Schaaffs obtained a velocity formula given by

$$c^2 = \gamma RT \left[\frac{\frac{1}{3}M}{(M - b\rho)^2} - \frac{2}{(M - b\rho)} \right] \quad (13)$$

He hypothesized the above expression for organic liquids

$$\left(\frac{\partial b}{\partial \rho} \right)_T = \frac{2M}{3\rho^2} \quad (14)$$

since

$$b = \frac{16}{3} \pi r_0^3 N \quad (15)$$

Molecular radius, r_0 , can be obtained from the equation

$$r_0 = \sqrt[3]{\frac{M}{\rho N}} \sqrt[3]{\frac{3}{16\pi} \left[1 - \frac{\gamma RT}{Mc^2} \left(\sqrt{1 + \frac{Mc^2}{3\gamma RT}} - 1 \right) \right]} \quad (16)$$

With the help of eqs (14) and (16) we have obtained the value of b as,

$$b = \frac{M}{\rho} - \frac{\gamma RT}{\rho c^2} \left[\sqrt{\left(\frac{Mc^2}{3\gamma RT} + 1 \right)} - 1 \right] \quad (17)$$

Since r_0 is independent of temperature, hence $b = b(T, \rho)$ will be independent of temperature i.e.

$$\left(\frac{\partial b}{\partial T} \right)_\rho = 0 \quad (18)$$

Assuming that, $x = \frac{V}{b} = \frac{M}{\rho b}$, from equation (13) we know that

$$c^2 = \left(\frac{\gamma RT}{M} \right) \frac{(6-5x)x}{3(x-1)^2} \quad (19)$$

where

$$x = \frac{V}{b} = \frac{M}{\rho b}$$

Differentiating equation (19), we get

$$dc^2 = \left[\frac{d\gamma}{\gamma} + \frac{dT}{T} + \frac{2(2x-3)}{(x-1)(6-5x)} \frac{dx}{x} \right] c^2 \quad (20)$$

$$\frac{dx}{x} = - \left[\frac{d\rho}{\rho} + \frac{db}{b} \right] \quad (21)$$

we get

$$dc^2 = \left[\frac{d\gamma}{\gamma} + \frac{dT}{T} - \frac{2(2x-3)}{(x-1)(6-5x)} \left(\frac{d\rho}{\rho} + \frac{db}{b} \right) \right] c^2 \quad (22)$$

On substituting eq (22) into eq (11) under adiabatic condition, we get

$$B/A = \rho c^2 \left\{ \frac{1}{\gamma} \left(\frac{\partial \gamma}{\partial \rho} \right)_s + \frac{1}{T} \left(\frac{\partial T}{\partial \rho} \right)_s - \frac{2(2x-3)}{(x-1)(6-5x)} \left[\frac{1}{\rho} \left(\frac{\partial \rho}{\partial \rho} \right)_s + \frac{1}{b} \left(\frac{\partial b}{\partial \rho} \right)_s \right] \right\} \quad (23)$$

We know that

$$\left(\frac{\partial b}{\partial \rho} \right)_s = \left(\frac{\partial b}{\partial \rho} \right)_s \left(\frac{\partial \rho}{\partial \rho} \right)_s = \left(\frac{\partial \rho}{\partial \rho} \right)_s \left[\left(\frac{\partial b}{\partial \rho} \right)_\tau - \left(\frac{\partial b}{\partial T} \right)_\rho \left(\frac{\partial S}{\partial \rho} \right)_\tau \left(\frac{\partial T}{\partial S} \right)_\rho \right] \quad (24)$$

For fluids,

$$c^2 = \left(\frac{\partial P}{\partial \rho} \right)_s \quad (25)$$

On substituting equations (16), (18), (24) and c^2 into equation (23), we get

$$B/A = \left(1 - \frac{1}{\gamma} \right) \frac{c^2 \rho \beta_T}{\alpha T} + \frac{2(3-2x)^2}{3(x-1)(6-5x)} \quad (26)$$

Tong and Dong derived this expression for B/A by using Schaaffs equation. For convenience above expression can be written as,

$$B/A = J_0 + J_{(x)} \quad (27)$$

where

$$J_{(0)} = \left(1 - \frac{1}{\gamma} \right) \left(\frac{c^2 \rho \beta_T}{\alpha T} \right) \quad (28)$$

$$= \left(1 - \frac{1}{\gamma} \right) \left(\frac{\gamma}{\alpha T} \right) \quad (29)$$

On simplification, we get

$$J_0 = \frac{\gamma - 1}{\alpha T} \quad (30)$$

$$J_{(x)} = \frac{2(3-2x)^2}{3(x-1)(6-5x)} \quad (31)$$

RESULTS AND DISCUSSION

Non linearity parameter of six binary systems diethylcarbonate + methanol (I), diethylcarbonate + ethanol (II), diethylcarbonate + 1-propanol (III), diethylcarbonate + 1-butanol (IV), diethylcarbonate + 2-butanol (V), diethyl carbonate + 1-pentanol (VI) at four temperatures 293.15 K, 298.15 K, 303.15 K, 313.15 K, and single ternary system ethyl acetate + n-hexane + acetone at 298.15K have been computed using thermodynamic method ²² (Tong and Dong), empirical relation ⁵ and expression derived by Hartmann ⁵ on the basis of intermolecular interaction. The experimental values of velocity and density have been taken from earlier papers.^{27, 28} The values of thermal expansion coefficient, adiabatic compressibility, isothermal compressibility and specific heat ratio of pure, binary and multicomponent systems are evaluated using eqs (3), (4), (5) and (6) respectively. The computed values of $J(0)$ and $J(x)$ and B/A at aforementioned temperatures for binary and ternary liquid mixtures are reported in Table-1 and Table-2 respectively.

Thermodynamic method developed by Tong and Dong has been employed to compute the values of B/A . The values of α , β and γ are evaluated by eqs (3), (5) and (6) respectively. With the help of these values, $J(0)$ and $J(x)$ are computed utilizing eqs (30) and (31). On further utilizing the values $J(0)$ and $J(x)$, B/A values have been calculated and are reported in columns 4, 5 and 6 of Table-1 respectively. A close perusal of this Table shows that in case of binary mixtures, the values of non-linearity parameter decrease with increase in concentration of the first component for system I at all the temperatures using Tong Dong method, whereas irregular variation in its values is observed in all the remaining systems under consideration. At higher x_1 values in of the most binary systems, B/A values are larger. At low concentration of diethyl carbonate its values are minimum. Second components in all the binary systems are alcohols containing strong interaction due to hydrogen bonding. Thus, B/A values are concerned with interactions between the components of binary systems.

Equations (1) and (2) have been used to evaluate B/A of aforementioned binary liquid mixtures using experimental velocity data and are reported in columns 7 and 8 of Table-1. Careful study of this Table shows that the values of non-linearity parameter increase with increase in temperature in each binary system under investigation. The values of non-linearity parameter decrease with increase in concentration of diethyl carbonate in systems I and II. At higher concentration of methanol and ethanol, deviation from linearity is larger and is smaller at their lower concentration. In remaining systems, B/A values increase with increase in concentration of the first component (diethyl carbonate). At higher concentration of 1-propanol, 1-butanol and 1-pentanol, values of non-linearity parameter are found smaller while at low concentration these are larger.

All the binary systems consist of alcohols as second component. At larger concentration of alcohol, hydrogen bonding produces dominating effect on ultrasonic propagation in mixtures. Binary systems of primary and branched chain alcohols with diethyl carbonate show reverse trend of B/A values. From this we can also conclude that at larger concentration of branched chain alcohol, B/A values are smaller while for systems having primary alcohols as higher concentration, its values are larger. Intermolecular interaction has dominating effect over ultrasonic velocity and density and hence on non-linearity values.

B/A values of ternary liquid mixture also have been calculated using eqs (1), (2) and (27) and are reported in Table-2. Maximum values of B/A have been observed when computation has been done using Hartmann relation, whereas minimum values are obtained using Tong Dong method mostly at all the concentrations. Irregular trend in values of non-linearity parameter is found for all the three approaches used in present work for the multi component systems.

Table 1. Non linearity parameter of binary liquid mixtures at various temperatures

diethyl carbonate (1) + methanol (2)

T=293.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0513	0.8172	1127	8.20	1.24	9.44	10.70	10.15
0.1002	0.8378	1136	8.38	1.22	9.60	10.63	10.06
0.1972	0.8699	1148	8.77	1.19	9.97	10.54	9.95
0.2839	0.8918	1157	9.12	1.17	10.29	10.47	9.87
0.4038	0.9150	1166	9.55	1.15	10.70	10.40	9.79
0.5000	0.9295	1171	9.86	1.14	11.00	10.37	9.75
0.5933	0.9411	1175	10.13	1.13	11.26	10.34	9.71
0.6417	0.9464	1178	10.26	1.13	11.39	10.32	9.69
0.7996	0.9608	1190	10.37	1.39	11.76	10.24	9.58

T=298.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0496	0.8116	1109	8.16	1.19	9.34	10.84	10.32
0.0996	0.8326	1117	8.33	1.17	9.49	10.77	10.24
0.1985	0.8652	1131	8.71	1.14	9.85	10.66	10.11
0.2944	0.8889	1140	9.07	1.12	10.19	10.60	10.03
0.4014	0.9093	1147	9.44	1.10	10.54	10.54	9.96
0.4975	0.9238	1153	9.73	1.09	10.83	10.50	9.91
0.6068	0.9372	1158	10.04	1.08	11.12	10.46	9.86
0.7087	0.9475	1165	10.29	1.07	11.37	10.41	9.80
0.8365	0.9581	1171	10.57	1.07	11.64	10.37	9.75

T=303.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0490	0.8065	1093	8.13	1.14	9.26	10.97	10.48
0.0966	0.8265	1100	8.28	1.12	9.40	10.91	10.41
0.1958	0.8592	1112	8.63	1.09	9.72	10.81	10.29
0.2824	0.8809	1122	8.94	1.08	10.01	10.73	10.20
0.3916	0.9021	1129	9.30	1.06	10.36	10.68	10.13
0.4936	0.9177	1134	9.60	1.05	10.65	10.64	10.08
0.5810	0.9286	1138	9.83	1.04	10.87	10.61	10.04
0.6945	0.9404	1143	10.11	1.03	11.14	10.57	10.00
0.7349	0.9441	1146	10.20	1.03	11.23	10.55	9.97
0.8512	0.9535	1152	10.45	1.02	11.47	10.51	9.92

T=313.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0509	0.7976	1062	8.00	1.05	9.05	11.23	10.80
0.0999	0.8175	1071	8.01	1.03	9.05	11.15	10.70
0.2009	0.8500	1084	8.15	1.01	9.16	11.04	10.57
0.2981	0.8735	1091	8.34	0.99	9.33	10.98	10.50
0.4009	0.8928	1095	8.54	0.97	9.51	10.95	10.46
0.5056	0.9083	1098	8.74	0.96	9.70	10.93	10.43
0.6062	0.9204	1101	8.91	0.95	9.86	10.90	10.40
0.7033	0.9301	1106	9.06	0.94	10.00	10.86	10.35
0.8055	0.9388	1112	9.21	0.94	10.15	10.81	10.29

diethyl carbonate (1) + ethanol (2)

T=293.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0503	0.8076	1163	10.03	1.27	11.30	10.43	9.82
0.0997	0.8238	1166	8.72	1.25	9.97	10.40	9.79
0.1980	0.8518	1171	9.00	1.22	10.22	10.37	9.75
0.3006	0.8762	1174	9.28	1.20	10.48	10.35	9.72
0.4031	0.8968	1177	9.55	1.18	10.72	10.33	9.70
0.5031	0.9141	1179	9.80	1.16	10.96	10.31	9.68
0.6063	0.9296	1183	10.05	1.15	11.20	10.28	9.64
0.6998	0.9407	1185	10.12	1.14	11.26	10.27	9.63
0.8066	0.9546	1190	10.52	1.13	11.64	10.24	9.58
0.8950	0.9642	1193	10.75	1.12	11.87	10.21	9.56

T=298.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0496	0.8029	1146	10.06	1.22	11.28	10.55	9.97
0.0973	0.8184	1148	10.83	1.20	12.03	10.54	9.95
0.1963	0.8464	1151	8.71	1.17	9.89	10.51	9.93
0.2985	0.8706	1154	8.00	1.15	9.15	10.49	9.90
0.3980	0.8905	1157	8.29	1.13	9.42	10.47	9.87
0.5057	0.9091	1160	9.26	1.11	10.37	10.45	9.84
0.6032	0.9237	1163	10.64	1.10	11.73	10.43	9.82
0.7035	0.9369	1166	12.65	1.09	13.74	10.40	9.79

T=303.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	$J(x)$	$J(0)$	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0491	0.7983	1129	10.09	1.17	11.26	10.68	10.13
0.0984	0.8142	1130	10.87	1.15	12.02	10.67	10.12
0.1952	0.8413	1133	8.76	1.12	9.89	10.65	10.09
0.2961	0.8650	1136	8.01	1.10	9.11	10.63	10.06
0.3946	0.8847	1138	8.25	1.08	9.33	10.61	10.04
0.4859	0.9005	1140	8.99	1.07	10.05	10.60	10.03
0.5995	0.9177	1143	10.49	1.05	11.54	10.57	10.00
0.6959	0.9305	1146	12.35	1.04	13.39	10.55	9.97

T=313.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	$J(x)$	$J(0)$	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0499	0.7897	1095	10.28	1.07	11.35	10.95	10.46
0.1020	0.8061	1096	11.03	1.05	12.08	10.94	10.45
0.2038	0.8339	1098	8.72	1.01	9.73	10.93	10.43
0.3116	0.8585	1099	8.00	0.98	8.98	10.92	10.42
0.4001	0.8755	1100	8.24	0.96	9.20	10.91	10.41
0.4971	0.8918	1102	9.00	0.94	9.93	10.89	10.39
0.6023	0.9072	1105	10.32	0.92	11.24	10.87	10.36
0.7058	0.9205	1107	12.19	0.90	13.09	10.85	10.34

diethyl carbonate (1) + 1-propanol (2)

T=293.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	$J(x)$	$J(0)$	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0504	0.8168	1219	8.42	1.29	9.70	10.04	9.34
0.1007	0.8293	1216	9.03	1.27	10.30	10.06	9.37
0.2008	0.8521	1210	8.43	1.24	9.68	10.10	9.42
0.3019	0.8725	1205	8.01	1.22	9.23	10.13	9.46
0.4004	0.8908	1201	8.20	1.20	9.40	10.16	9.49
0.5039	0.9082	1198	8.94	1.18	10.12	10.18	9.52
0.6031	0.9235	1197	10.17	1.16	11.33	10.19	9.53
0.7007	0.9375	1196	12.02	1.15	13.17	10.19	9.53

T=298.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	$J(x)$	$J(0)$	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0515	0.8127	1201	8.47	1.23	9.70	10.16	9.49
0.0993	0.8244	1198	9.07	1.22	10.29	10.18	9.52
0.2021	0.8473	1191	8.47	1.19	9.66	10.23	9.58
0.3007	0.8674	1186	8.01	1.17	9.18	10.26	9.62
0.4026	0.8860	1182	8.19	1.15	9.33	10.29	9.65
0.5022	0.9026	1179	8.87	1.13	10.00	10.31	9.68
0.6029	0.9180	1177	10.08	1.11	11.19	10.33	9.70
0.7041	0.9324	1177	11.95	1.10	13.05	10.33	9.70

T=303.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0464	0.8073	1185	8.37	1.18	9.56	10.27	9.63
0.0963	0.8194	1181	9.07	1.17	10.24	10.30	9.66
0.1968	0.8418	1174	8.51	1.14	9.65	10.35	9.72
0.2981	0.8621	1168	8.02	1.12	9.14	10.39	9.77
0.3987	0.8804	1164	8.16	1.10	9.26	10.42	9.81
0.4958	0.8965	1161	8.79	1.08	9.87	10.44	9.84
0.5991	0.9123	1158	9.98	1.06	11.04	10.46	9.86
0.6967	0.9260	1157	11.69	1.05	12.74	10.47	9.87

T=313.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0506	0.7811	1086	9.48	1.08	10.56	11.02	10.55
0.0997	0.7933	1086	11.73	1.07	12.79	11.02	10.55
0.2016	0.8172	1087	10.22	1.04	11.26	11.02	10.54
0.3030	0.8390	1088	8.46	1.02	9.48	11.01	10.53
0.4008	0.8582	1091	8.00	1.00	9.00	10.98	10.50
0.4969	0.8759	1093	8.25	0.99	9.24	10.97	10.48
0.5990	0.8932	1097	9.09	0.97	10.07	10.93	10.44
0.7007	0.9093	1101	10.57	0.96	11.53	10.90	10.40
0.8011	0.9243	1105	12.95	0.95	13.89	10.87	10.36

diethyl carbonate (1) + 1-butanol (2)

T=293.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0510	0.8201	1251	8.07	1.30	9.37	9.83	9.09
0.1027	0.8305	1244	8.52	1.28	9.80	9.88	9.15
0.2008	0.8493	1234	8.40	1.26	9.66	9.94	9.22
0.2978	0.8670	1225	8.04	1.23	9.27	10.00	9.30
0.4026	0.8853	1217	8.10	1.21	9.31	10.05	9.36
0.8079	0.9027	1211	8.40	1.19	9.59	10.09	9.41
0.6014	0.9175	1206	9.64	1.17	10.82	10.13	9.45
0.7033	0.9329	1203	11.36	1.15	12.52	10.15	9.48
0.7986	0.9468	1201	13.97	1.14	15.11	10.16	9.49

T=298.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0519	0.8162	1234	8.09	1.25	9.33	9.94	9.22
0.0993	0.8255	1228	8.52	1.23	9.75	9.98	9.27
0.1996	0.8445	1216	8.42	1.21	9.63	10.06	9.37
0.2923	0.8614	1208	8.06	1.18	9.24	10.11	9.43
0.3989	0.8798	1199	8.08	1.16	9.24	10.17	9.51
0.5017	0.8967	1193	8.60	1.14	9.74	10.21	9.56
0.6016	0.9124	1187	9.60	1.12	10.72	10.26	9.61
0.7043	0.9278	1184	11.31	1.10	12.41	10.28	9.64
0.8002	0.9416	1181	13.87	1.09	14.96	10.30	9.66

T=303.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0508	0.8120	1216	8.07	1.19	9.27	10.06	9.37
0.1004	0.8217	1210	8.51	1.18	9.69	10.10	9.42
0.2016	0.8407	1198	8.40	1.15	9.55	10.18	9.52
0.3000	0.8583	1188	8.04	1.13	9.17	10.25	9.60
0.3917	0.8739	1181	8.06	1.11	9.17	10.30	9.66
0.5032	0.8920	1173	8.59	1.09	9.68	10.35	9.73
0.5970	0.9066	1169	9.51	1.07	10.59	10.38	9.77
0.7099	0.9233	1164	11.35	1.05	12.40	10.42	9.81

T=308.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0506	0.8037	1181	8.09	1.10	9.19	10.30	9.66
0.1007	0.8132	1172	8.54	1.09	9.63	10.36	9.74
0.2005	0.8314	1160	8.44	1.06	9.50	10.45	9.84
0.2975	0.8483	1150	8.06	1.04	9.10	10.52	9.93
0.4122	0.8674	1142	8.09	1.02	9.11	10.58	10.01
0.5035	0.8818	1136	8.53	1.00	9.53	10.63	10.06
0.6084	0.8978	1131	9.54	0.98	10.52	10.66	10.11
0.7044	0.9118	1126	11.04	0.97	12.00	10.70	10.16
0.8055	0.9259	1122	13.54	0.95	14.49	10.73	10.20

diethyl carbonate(1)+2-butanol(2)

T=293.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0512	0.8166	1223	8.13	1.29	9.42	10.01	9.31
0.1031	0.8267	1218	8.76	1.28	10.03	10.05	9.35
0.2021	0.8453	1209	8.65	1.25	9.90	10.11	9.43
0.2997	0.8631	1203	8.13	1.23	9.35	10.15	9.48
0.4023	0.8811	1198	8.03	1.21	9.23	10.18	9.52
0.5115	0.8993	1196	8.48	1.19	9.67	10.19	9.53
0.6070	0.9148	1195	9.38	1.17	10.55	10.20	9.54
0.7070	0.9305	1194	10.79	1.15	11.94	10.21	9.55
0.8038	0.9453	1195	13.26	1.14	14.40	10.22	9.56

T=298.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0509	0.8122	1205	8.13	1.24	9.37	10.13	9.46
0.1010	0.8217	1200	8.77	1.22	9.99	10.17	9.50
0.2020	0.8405	1191	8.69	1.20	9.89	10.23	9.58
0.3002	0.8582	1184	8.14	1.18	9.32	10.28	9.64
0.4040	0.8762	1179	8.02	1.15	9.18	10.31	9.68
0.5003	0.8923	1176	8.38	1.14	9.52	10.33	9.70
0.6008	0.9086	1174	9.26	1.12	10.38	10.35	9.72
0.6963	0.9236	1174	10.70	1.10	11.80	10.35	9.72

T=303.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0517	0.8084	1189	8.14	1.19	9.33	10.24	9.59
0.1132	0.8200	1182	8.84	1.17	10.00	10.29	9.65
0.2267	0.8407	1172	8.52	1.14	9.67	10.36	9.74
0.3316	0.8591	1166	8.05	1.12	9.17	10.40	9.79
0.4467	0.8786	1160	8.12	1.10	9.22	10.45	9.84
0.5422	0.8942	1157	8.67	1.08	9.75	10.47	9.87
0.6426	0.9101	1155	9.77	1.06	10.83	10.48	9.89
0.7416	0.9253	1154	11.59	1.05	12.63	10.49	9.90

T=313.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0511	0.7989	1150	8.17	1.09	9.26	10.52	9.93
0.1026	0.8083	1143	8.88	1.07	9.95	10.57	10.00
0.1988	0.8256	1133	8.83	1.04	9.87	10.65	10.09
0.2955	0.8425	1126	8.22	1.01	9.23	10.70	10.16
0.4041	0.8602	1120	8.00	0.98	8.98	10.75	10.21
0.5084	0.8779	1116	8.34	0.96	9.30	10.78	10.25
0.5983	0.8921	1115	9.06	0.93	9.99	10.79	10.26
0.6988	0.9076	1114	10.43	0.91	11.34	10.80	10.27
0.8034	0.9233	1113	12.84	0.89	13.73	10.81	10.28

diethyl Carbonate(1)+1-pentanol(2)

T=293.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0496	0.8228	1286	8.00	1.31	9.32	9.62	8.83
0.1016	0.8316	1278	8.20	1.30	9.50	9.67	8.89
0.2034	0.8486	1263	8.28	1.27	9.56	9.76	9.00
0.3124	0.8665	1249	8.03	1.25	9.27	9.85	9.11
0.3801	0.8775	1241	8.01	1.23	9.25	9.90	9.17
0.5085	0.8981	1228	8.49	1.20	9.69	9.98	9.27
0.6047	0.9133	1220	9.35	1.18	10.53	10.03	9.34
0.7068	0.9293	1214	10.93	1.16	12.09	10.07	9.38
0.8058	0.9447	1208	13.56	1.14	14.71	10.11	9.43

T=298.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0459	0.8186	1269	8.02	1.26	9.28	9.72	8.96
0.0984	0.8273	1262	8.18	1.25	9.43	9.77	9.01
0.2067	0.8451	1246	8.27	1.22	9.49	9.87	9.13
0.3012	0.8604	1233	8.04	1.20	9.24	9.95	9.23
0.4002	0.8762	1221	8.04	1.17	9.22	10.03	9.33
0.5091	0.8934	1209	8.48	1.15	9.63	10.11	9.43
0.5884	0.9058	1202	9.14	1.13	10.27	10.15	9.48

T=303.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0541	0.8158	1249	8.00	1.21	9.21	9.85	9.11
0.0951	0.8225	1242	8.17	1.19	9.36	9.89	9.16
0.1968	0.8390	1226	8.30	1.15	9.45	9.99	9.29
0.2920	0.8542	1213	8.07	1.12	9.19	10.08	9.39
0.3986	0.8711	1200	8.03	1.09	9.12	10.17	9.50
0.4966	0.8865	1190	8.39	1.06	9.45	10.24	9.58
0.5963	0.9020	1181	9.19	1.03	10.22	10.30	9.66
0.6847	0.9156	1175	10.40	1.01	11.41	10.34	9.71
0.7988	0.9329	1168	13.05	0.98	14.03	10.39	9.77

T=313.15K

x_1	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.0505	0.8073	1214	8.00	1.11	9.11	10.07	9.38
0.1009	0.8152	1205	8.21	1.09	9.30	10.13	9.46
0.2038	0.8312	1187	8.31	1.06	9.37	10.26	9.61
0.3044	0.8468	1173	8.06	1.03	9.08	10.35	9.73
0.4054	0.8623	1161	8.03	1.00	9.03	10.44	9.84
0.5077	0.8781	1150	8.40	0.97	9.37	10.52	9.93
0.5969	0.8916	1143	9.10	0.95	10.04	10.57	10.00
0.7100	0.9086	1134	10.65	0.92	11.57	10.64	10.08
0.8100	0.9236	1127	13.07	0.90	13.97	10.70	10.15

Table 2. Non linearity parameter of ternary liquid mixture at 298.15K

ethyl acetate (1) + hexane (2) +acetone (3)								
x ₁	x ₂	ρ gm cm ⁻³	c ms ⁻¹	J(x)	J(0)	B/A eq (27)	B/A eq (1)	B/A eq (2)
0.4430	0.5060	0.7451	1078	9.28	1.24	10.52	11.09	10.63
0.3716	0.5855	0.7279	1070	8.44	1.26	9.70	11.16	10.71
0.2777	0.6903	0.7069	1067	8.03	1.28	9.31	11.18	10.75
0.1920	0.7859	0.6892	1065	8.04	1.30	9.34	11.20	10.77
0.1011	0.8872	0.6721	1066	8.37	1.32	9.69	11.19	10.76
0.7066	0.1138	0.8403	1142	8.02	1.17	9.19	10.58	10.01
0.6284	0.2119	0.8116	1116	8.00	1.19	9.19	10.78	10.25
0.5563	0.3023	0.7873	1100	8.00	1.21	9.21	10.91	10.41
0.4795	0.3986	0.7637	1088	8.02	1.23	9.25	11.01	10.53
0.4072	0.4893	0.7432	1078	8.06	1.24	9.31	11.09	10.63
0.3130	0.6074	0.7190	1071	8.16	1.27	9.43	11.15	10.70
0.4189	0.3947	0.7579	1089	11.20	1.23	12.43	11.00	10.52
0.3529	0.4900	0.7373	1078	10.47	1.25	11.72	11.09	10.63
0.2710	0.6085	0.7142	1071	9.84	1.27	11.11	11.15	10.70

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